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Synthesis and Analysis of Jet Fuel from Shale Oil and Coal Syncrudes

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16. Abstract

Thirty-two jet fuel samples of varying properties were produced from shale oil and coal syncrudes, and analyzed to assess their suitability for use. TOSCO II shale oil and H-COAL and COED syncrudes were used as starting materials. The processes used were among those commonly in use in petroleum processing—distillation, hydrogenation and catalytic hydrocracking. The processing conditions required to meet two levels of specifications regarding aromatic, hydrogen, sulfur and nitrogen contents at two yield levels were determined and found to be more demanding than normally required in petroleum processing. Analysis of the samples produced indicated that if the more stringent specifications of 13.5% hydrogen (min.) and 0.02% nitrogen (max.) were met, products similar in properties to conventional jet fuels were obtained. In general, shale oil was easier to process (catalyst deactivation was seen when processing coal syncrudes), consumed less hydrogen and yielded superior products. Based on these considerations, shale oil appears to be preferred to coal as a petroleum substitute for jet fuel production.

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I. SUMMARY

Within the broad range objective of evaluation of alternative hydrocarbon sources to crude petroleum, the specific objective of this program was the production and analysis of jet fuel samples of various properties from shale oil and coal syncrudes.

One shale oil (TOSCO II) and two coal syncrudes (H-COAL and COED) were used as starting materials. The processes used were among those commonly in use in petroleum processing—distillation, hydrogenation and catalytic hydrocracking.

The sample properties which were varied on a controlled basis were boiling range and percent hydrogen and nitrogen. Aromatics content and percent sulfur also varied as a result. The amount of jet fuel produced from a given amount of syncrude also was varied. In one case, the 311-616^{o}K (100-650^{o}F) boiling range material existing in the syncrude was hydrotreated to meet specifications. The yield was then augmented by hydrocracking some of the heavier syncrude fractions to 616^{o}K (650^{o}F) and lighter products.

The processing conditions required to make various specification products were determined and found to be considerably more severe than are normally required in petroleum processing. In particular, the amount of catalyst required, pressure and hydrogen consumption were unusually high. Space velocities of 0.3-1.0 and hydrogen pressures in the 13.8-17.2 x 10^6 N/m^2 (2000-2500 PSIG) range were generally necessary, as compared to the more usual ranges of 1-4 space velocity and 3.45-6.90 x 10^6 N/m^2 (500-1000 PSIG). Thirty-two .0076 m^3 (two gallon) samples of various properties were prepared and analyzed to assess their suitability for use as jet fuel. The program demonstrated that products which may be useful as jet fuels can be made from these petroleum substitutes by hydrotreating and hydrocracking to meet the more stringent of the specifications used in the program of 13.5% hydrogen (min.) and 0.02% nitrogen (max.). If these are met, the additional specifications of 0.2% sulfur (max.) and 20% aromatics (max.) were also easily satisfied. Hydrogen consumption ranged from 185 to 388 m^3/m^3 (1100 to 2300 SCF/B), two to four times the normal values when processing petroleum derived stocks.

In general, shale oil was easier to process (catalyst deactivation was seen when processing coal syncrudes) and yielded superior products, primarily in terms of smoke point. Hydrogen consumption with shale oil was substantially lower also, particularly if calculated using coal as the starting material.

Technical and economic optimization of these processes was not a part of this program, but it appears that shale oil would be preferred to coal as the original hydrocarbon source for jet fuel production.

II. INTRODUCTION

As a result of currently declining supplies of domestic crude petroleum, which ultimately will become world-wide, potential alternate hydrocarbon sources are being evaluated for the production of jet fuel. In this program one shale oil and two coal syncrudes were used as starting materials for production of jet fuel samples of varying properties. These samples were extensively analyzed, and .0038 m^3 (one gallon) portions of each were furnished to the NASA Lewis Research Center for their further evaluation.

The sample specifications included boiling range (initial boiling point defined by vapor pressure and flash point), content of aromatics, hydrogen, nitrogen and sulfur, and yield of product. Yields were based on the portion of the product boiling in the range of 422-561°K (300-550°F), and samples were to be produced at two levels, 20 and 40 wt. % (min.) based on starting syncrude. At each yield level, a 311-616°K (100-650°F) fraction was to be produced at high and low processing severities so as to conform with the following specifications:

	Low Severity	High Severity
Vol. % Aromatics (max.)	40	20
Wt. % Hydrogen (min.)	12.75	13.50
Wt. % Sulfur (max.)	0.5	0.2
Wt. % Nitrogen (max.)	0.2	0.1

Each of these 311-616°K (100-650°F) boiling range products were then to be distilled as required to produce final product samples of the following volatility specifications:

	1	2	3	4
Flash Point (min.)	-	311°K (100°F)	-	311°K (100°F)
Reid Vapor Pressure (max.)	2×10^4 N/m^2 (3 psi)	-	2×10^4 N/m^2 (3 psi)	-
ASTM Final Boiling Point (max.)	561°K (550°F)	561°K (550°F)	616°K (650°F)	616°K (650°F)

This resulted in a total requirement of thirty-two different samples.

The processes used to produce these samples were to be conventional processes such as would be used in the production of jet fuel from crude petroleum; those used were distillation, hydrogenation and catalytic hydrocracking. Some test data were also obtained on delayed coking, but this process was not used in the actual preparation of the samples.

Other work has also been performed in the same general area[1,2,3,4], but this program is not directly related, except in that some previous work performed in this facility[4] was used to initially define the general processing scheme and conditions for the coal syncrude phase.

III. SHALE OIL

A. Experimental Procedure

1. Feedstock Preparation and Analysis

For the shale oil phase of the program, the starting material was a sample of full range shale oil prepared in the TOSCO II process pilot plant. Analyses obtained on this material are shown in Table II. (Analytical methods used in this program are shown in Table I). To prepare the necessary fractions for further analysis and for processing, a charge of 533.9 Kg (1177 lbs.) was fractionated successively in a .203 m (8") dia. and a .102 m ([illegible]") dia. still to produce cuts of 311-422 (100-300), 422-561 (300-550), 561-616 (550-650), 616-700 (650-800), and 700°K+ (800°F+) TBP. Analyses of these cuts are also shown in Table II. The 700°K+ (800°F+) bottoms fraction was then further separated into 700-783 (800-950) and 783°K+ (950°F+) fractions in a continuous vacuum flash still. A plot of wt. % overhead vs. temperature, calculated from these fractionations and corrected for losses, is shown in Figure 1. These cuts were then composited to produce a 311-616°K (100-650°F) stock for direct hydrotreating to the jet fuel specifications, and a 616-783°K (650-950°F) feedstock for hydrocracking to increase the jet fuel yield from the original shale oil.

2. Hydrotreating of Shale Oil Fractions

The initial hydrotreating work on the IBP-616°K (650°F) and the 616-783°K (650-950°F) shale oil fractions involved short experimental programs to determine the processing conditions necessary to meet product requirements. Based on previous experience, the nitrogen level was identified as the controlling product specification for treating this shale syncrude, and processing conditions were selected and adjusted during both experimental and production runs on this basis.

The feed was treated in a .025 m (1") diameter isothermal, continuous flow reactor over .06 Kg of American Cyanamid HDS-3A, a commercial .0016 m (1/16") Ni-Mo/Al_2O_3 catalyst. The catalyst was uniformly diluted 2:1 with tabular alumina to form a .51 m (20 inch) packed bed. A fresh charge of catalyst was used for each feed. Tests were conducted over a range of operating conditions so that a trend could be established relating product nitrogen level to processing severity. When the necessary process conditions had been defined, large scale production runs (∿.076 m^3, ∿20 gals. product) were made on both feedstocks in .051 m (two inch) diameter reactors. The same type of NiMo catalyst was used for both runs. All catalyst charges were presulfided with a 10% H_2S/90% H_2 blend before processing was initiated.

TABLE I

ANALYTICAL METHODS USED IN PROGRAM

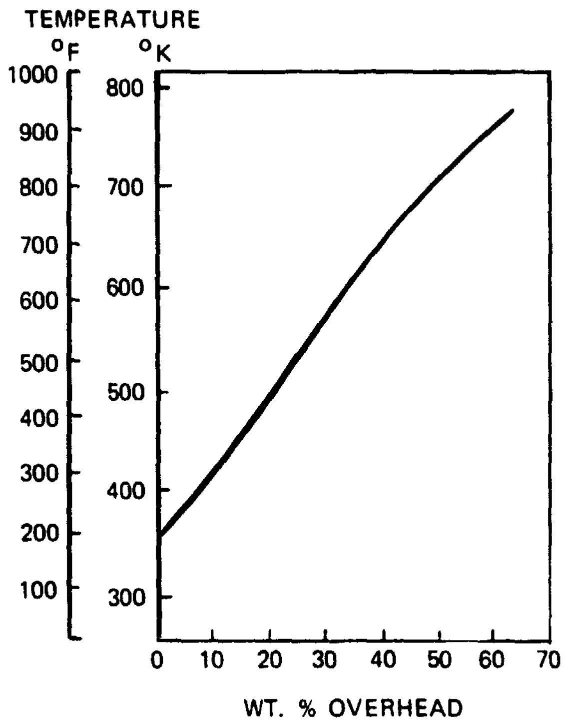
METHOD	ABBREVIATION
WT. % CARBON, COMBUSTION	% C
WT. % HYDROGEN, COMBUSTION	% H
WT. % SULFUR, X-RAY FLUORESCENCE	% S
p.p.m. SULFUR, DOHRMANN	ppm S
WT. % NITROGEN KJELDAHL	% (ppm) N
WT. % OXYGEN, UNTERZAUCHER	% O
GRAVITY, °API (ASTM D-287)	°API
SPECIFIC GRAVITY 60/60 (ASTM D-1217)	SPECIFIC GRAVITY
DISTILLATION, ATM. (ASTM D-86)	DIST. D-86
DISTILLATION, VAC. (ASTM D-1160)	DIST. D-1160
DISTILLATION, SIMULATED TBP BY GAS CHROMATOGRAPHY	G.C. DIST.
REID VAPOR PRESSURE (ASTM D-323)	R.V.P.
FLASH POINT (ASTM D-56)	FLASH PT.
KINEMATIC VISCOSITY (ASTM D-88)	KV
SAYBOLT VISCOSITY (ASTM D-445)	SFS
PENTANE INSOLUBLES	C_5 INSOL.
WT. % ASH (ASTM D-482)	
% MONOCYCLIC, % POLYCYCLIC, AROMATICS, % NAPHTHALENES – COMBINATION CHROMATOGRAPHY AND MASS SPECTROMETER	NONE
% AROMATICS (ASTM D-1319)	% AROM.
% OLEFINS (ASTM D-1319)	% OLEF.
NET HEAT OF COMBUSTION (ASTM D-2382)	NET HEAT COMB.
EXISTING GUM (ASTM D-381)	EXISTING GUM
THERMAL STABILITY (ASTM D-3241)	THERMAL STAB.
SMOKE POINT (ASTM D-1322)	SMOKE PT.
FREEZING POINT (ASTM D-2386)	FREEZING PT.
POUR POINT (ASTM D-97)	POUR PT.
RING & BALL SOFTENING POINT (ASTM D-36)	RING & BALL SOFTENING PT.
REFRACTIVE INDEX @ 20°C (ASTM D-1218)	R. I. @ 20°C
WT. % CHLORINE, WET ANALYSIS	% Cl

TABLE II

TOSCO II SHALE OIL ANALYSES

Drum No.	D-3630	–	D-3633	D-3634	D-3635	D-3643		–
Sample No. J-	33227	33234	33239	33236	33237	33245		33254
Fraction, °K	Total	Wet Gas	IBP-425	425-561	561-616	616-700	700-783	700+
(°F)			(IBP-305)	(305-550)	(550-650)	(650-800)	(800-950)	(800+)
Yield, Wt. %	100.0	0.68	9.37	18.41	6.56	12.10	19.0	52.88
Gravity, Kg/m^3 (°API)	939.6 (19.1)		774.9 (51.1)	861.2 (32.8)	920.0 (22.3)	937.7 (19.4)		
Sp. Gr. 60/60, g/ml								1.0301
% C	83.88		86.83	84.58	84.68	85.38		85.83
% H	10.74		13.17	12.14	11.37	11.32		9.58
% S	0.683		0.770	0.735	0.673	0.643		0.53
% N	2.10		0.3915	1.39	2.12	1.96		2.67
% O	1.23		0.78	1.26	1.35	1.13		1.63
Pour Pt., °K (°F)	277 (40)							
KV/o cS			1.251	10.58				
KV/100 cS	29.23			2.110	12.21	48.76		
KV/210 cS	4.34				2.431	5.232		
SFS/210cS								62.73
NC_5 Insol., WT. %								20.732
% Ash	0.007		0.0	0.0	0.0	0.0		0.04
Monocyclic Aromatics, Vol. %			15.9	28.4	12.9	11.3		5.8
Polycyclic Aromatics, Vol. %			0.2	4.4	14.6	17.5		12.2

FIGURE 1
TOSCO II
FULL RANGE SHALE OIL
DISTILLATION CURVE



a. <u>311-616°K (100-650°F) Shale Oil Fraction</u>

The following matrix of operating conditions was chosen for the preliminary investigation as a range likely to yield products meeting the required specifications:

Temperature, °K	630-658 (675-725°F)
Pressure, N/m^2	13.8×10^6 (2000 PSIG)
WHSV*	0.5-1.0
H_2 Rate, m^3/m^3**	1.35×10^3 (8000 SCF/B†) (no recycle)

*Weight hourly space velocity, g. feed/hr./g. catalyst.

**Cubic meters @ 273°K, 10.1×10^4 N/m^2 per cubic meter of feed.

†Standard Cubic Feet @ 60°F. 760 mm Hg. per 42 gal. barrel of feed.

The results of these tests were used to estimate processing severities required to meet the two product quality levels for the production run. A .300 Kg catalyst charge was used, and for the low severity operation (∿0.2% N product) a reactor temperature of 616°K (650°F) and a WHSV of 1.5 hr^{-1} were chosen as initial conditions. Pressure was maintained at 13.8×10^6 N/m^2 (2000 PSIG) and once-through hydrogen rate at 1350 m^3/m^3 (8000 SCF/B). These conditions were ∿25 percent more severe than the experimental study indicated to be necessary to achieve the specified maximum product nitrogen level of 0.2%. Initial products, however, did not meet requirements and it was necessary to increase the temperature to 625°K (665°F) for the remainder of the low severity operation.

Since denitrogenation of this material did not prove excessively difficult, the objective of the high severity operation was changed with the concurrence of NASA to a 0.02% product nitrogen level rather than the 0.1% originally intended. Following the low severity segment of the run, the temperature was increased to 652°K (715°F) to make the second product. Approximately .076 m^3 (20 gallons) of feed were treated at each of the two severity levels.

b. 616-783^{o}K (650-950^{o}F) Shale Oil Fraction

Since the purpose of this processing step was to prepare this fraction for a subsequent hydrocracking step, a product nitrogen level of 400 ppm or less was required. The preliminary experimental program covered the following range of process variables:

Temperature, ^{o}K	644-666 (700-740^{o}F)
Pressure, N/m^2	13.8 x 10^6 (2000 PSIG)
WHSV	0.75-0.33
H_2 Rate, m^3/m^3	1350 (8000 SCF/B)

Based on the results of these tests, processing conditions for the production run were initially set at 663^{o}K (740^{o}F), 0.43 WHSV, 13.8 x 10^6 N/m^2 (2000 PSIG) and 1350 m^3/m^3 (8000 SCF/B) hydrogen rate. This run used a .700 Kg charge of NiMo catalyst.

Initial results from this run, as in the 311-616^{o}K (100-650^{o}F) feed run, again showed that the conversion obtained with this catalyst charge was somewhat lower than noted during the experimental run. In order to achieve the proper product nitrogen level, it was therefore necessary to increase the temperature to 675^{o}K (755^{o}F) and reduce the WHSV to 0.36. Operation at these severe conditions resulted in deactivation of the catalyst during the course of the run. Approximately 20-25% of the initial catalyst activity was lost during the 309 hours of operation. A total of .068 m^3 (18 gallons) of product was obtained from this run, with a nitrogen content of 233 ppm.

3. Hydrocracking of Denitrogenated 616-783^{o}K (650-950^{o}F) Shale Oil Fraction

The hydrocracking process was conducted in a single stage hydrocracking pilot plant, consisting of two reactors in series. The first reactor was charged with hydrodenitrogenation (HDN) catalyst to further reduce the feed organic nitrogen content from 233 ppm to 50 ppm. The total effluent (gas and liquid) from this reactor was then passed over the hydrocracking catalyst in the second reactor, where the hydrocracking reactions take place. Both catalysts employed in this process are proprietary, and are commercially available under license.

In order to determine the conditions necessary to yield a suitable organic nitrogen level in the feed to the hydrocracking zone and to obtain suitable hydrocrackate yields, short process variable programs were run prior to the production run. Process variable work was run first in the hydrotreating zone while the hydrocracking zone was being conditioned by passing the effluent gas from the hydrotreating zone over the hydrocracking catalyst. This equilibrates the hydrocracking catalyst with the ammonia and hydrogen sulfide in this gas stream. The hydrocracking process variable work was then done using the complete single stage system. Pressure was fixed at 13.8×10^6 N/m^2 (2000 PSIG), H_2 rate at 1685 m^3/m^3 (10,000 SCF/B), and space velocity set to minimize conversion of feed to 311^{o}K (100^{o}F) and lighter in the hydrotreater and maximize the 311-616^{o}K (100-650^{o}F) yield in the hydrocracker. Process temperatures for the hydrotreating runs varied between 625 (665) and 652^{o}K (715^{o}F), and based upon the results of these tests the processing conditions were set at 639^{o}K (690^{o}F) and 1 WHSV.

Process conditions for the hydrocracking zone in the experimental single stage tests were 616-630^{o}K (650-675^{o}F) and 1.0 WHSV. The shale gas oil was easier to hydrocrack than had been anticipated and only the lowest temperature produced a conversion to 616^{o}K- (650^{o}F$^-$) low enough to use for planning. Based on this point and an assumed activation energy of 2.5×10^8 joule/Kg. mole (60 kcal/gm. mole), the process conditions were set at 622^{o}K (660^{o}F) and 0.75 WHSV for 80% conversion to 616^{o}K (650^{o}F) and lighter.

The production run was performed using .051 m (2") I.D. reactors; the hydrodenitrogenation reactor contained .300 Kg of catalyst and the hydrocracking reactor contained .400. Both were diluted with inert tabular alumina, with a constant catalyst/diluent ratio throughout the bed, ($\sim$.001 m^3). Due to the limitations of time and feedstock quantity, the activity of the hydrocracking catalyst was not completely stabilized, and the initial portion of the production run was done while this catalyst retained a high flush activity. Because of this high activity, the temperature in the hydrocracking zone had to be lowered to obtain the desired conversion level. As the flush activity diminished the temperature was raised up to the initially determined 616^{o}K (650^{o}F). During this period of flush activity, some overcracking occurred, resulting in higher than normal losses to 311^{o}K (100^{o}F) and lighter products. About .061 m^3 (16 gals.) of feed were processed in this manner.

4. Final Blending and Fractionation of Shale Oil Products

The hydrocracked 616-783°K (650-950°F) shale oil was fractionated in a .051 m (2"), 15 plate vacuum jacketed glass column to produce 311-616° (100-650°) and 616°K+ (650°F+) fractions. In order to make the high yield samples, portions of this fraction were blended with portions of the high and low nitrogen 311-616°K (100-650°F) hydrotreated products in a ratio of 31.5% hydrocrackate/68.5% 311-616°K (100-650°F) HDN product, which is in yield proportion to the feed fractions. The low yield samples consist solely of the hydrotreated 311-616°K (100-650°F) HDN products. The four 311-616°K (100-650°F) hydrotreated products (i.e., low yield-high N; low yield-low N; high yield-high N and high yield-low N) were then fractionated in the .051 m (2 inch) distillation column to produce the final samples. Two fractionations were required to produce four samples from each 311-616°K (100-650°F) product. The 2×10^4 N/m² (3 psi) RVP/616°K EP specification was satisfied by the unfractionated material. The first fractionation removed the 394°K (250°F)- fraction to meet the 311°K (100°F) flash/616°K E.P. spec. In the second, appropriate overhead cuts were taken and blended back to meet the 2×10^4 N/m² (3 psi) RVP/561°K (550°F) EP and 311°K (100°F) flash/561°K EP specs.

5. Delayed Coking of 783°K (950°F)+ Shale Oil Bottoms

In order to obtain an estimate of the additional yield that could be obtained if the 783°K (950°F)+ bottoms were processed by delayed coking, a run was made in a pilot plant at typical commercial coker conditions: 721°K (839°F) drum temperature, 27.6×10^4 N/m² (40 PSIG) drum pressure, 1.1/1.0 recycle ratio (total feed/fresh feed) and a flash still recycle cut point of 714-727°K (825-850°F), which is equivalent to a TBP end point of ∿755°K (∿900°F). Fresh feed rate was .848 Kg./hour (.933 Kg/hour combined feed) for a total of 4.240 Kg during the 5 hour run period.

B. Results

1. Hydrotreating

a. 311-616°K (100-650°F) Shale Oil

The HDN results from the experimental and production runs on the 311-616°K (100-650°F) fraction of shale oil are shown in Figure 2. This is a first order kinetics representation, in which the log of feed nitrogen content/product nitrogen content is plotted against a severity factor. This severity factor is the product of 1/WHSV and a temperature factor (F_T, Figure 3), which corrects data at other temperatures to 644°K (700°F). The temperature factor is obtained by determining the ratio of space velocities required to obtain the same conversion at a temperature, T_N, relative to a baseline temperature, T_O. In this case, $F_{T_N} = \frac{WHSV(T_N)}{WHSV(644°K)}$ at constant conversion. Comparison of the two lines for the experimental and production runs clearly shows the difference in operating severity required to obtain a given nitrogen level. This difference in required severity is equivalent to an effective overall catalyst activity in the production run of ~60% of that observed in the preliminary run. Possible explanations for this might be poorer catalyst contacting in the larger diameter reactor or a less effective initial activation of the catalyst charge. From the slope of the line in Figure 3, the overall apparent activation energy for the denitrogenation reactions was calculated as 1.07×10^8 joule/Kg. mol (25.6 kcal/g. mol). An increase in temperature of ~22°K (~40°F) will double the reaction rate.

No loss of activity was observed during the length of the production run. The three points plotted on Figure 2 at greater than 1500 ppm product nitrogen represent both start and finish of the low severity portion of the run. The point at 120 ppm was obtained well into the high severity segment. All line up well on the correlation trend. The two points between 200 and 500 ppm came at the start of high severity operation. Apparently the catalyst surface had not yet completely equilibrated with the feed at the new higher temperature and these points represent a lineout period.

The analyses of the 311-616°K (100-650°F) shale oil feed and the composite of the low and high severity production runs are shown in Table III. As anticipated, all other specifications for hydrotreated products were easily met. Hydrogen consumed in the preparation of these two products was 158 and 185 m^3/m^3 (940 and 1100 SCF/B), respectively.

b. <u>616-783°K (650-950°F) Shale Oil</u>

The results of the experimental and production HDN runs on the 616-783°K (650-950°F) fraction of shale oil, preparatory to the hydrocracking step, are shown in Figure 4. As with the 311-616°K (100-650°F) cut data, a first order kinetic representation is used, but with an added correction factor in the severity term for catalyst activity (α). Defined on a relative space velocity basis to a standard activity, α_0, i.e.,

$$\alpha_N = \frac{\mathrm{WHSV}(\alpha_N)}{\mathrm{WHSV}(\alpha_0)} \quad \text{at constant conversion.}$$

The effect of temperature on nitrogen removal is shown in the form of an Arrhenius plot in Figure 5. The apparent overall activation energy is 1.66×10^8 joule/Kg mole (39.6 Kcal/g mole), corresponding

TABLE III

FEED AND PRODUCT INSPECTIONS

IBP–616°K (650°F) SHALE SYNCRUDE

	FEED, D-3638		LOW SEVERITY PRODUCT		HIGH SEVERITY PRODUCT	
SAMPLE NO. J–	33240		33279		33286	
GRAVITY, Kg/M^3 (°API)	845.8 (35.8)		804.0 (44.5)		797.6 (45.9)	
HYDROGEN, %	12.26		13.64		13.82	
SULFUR, %	0.699		.001		.001	
NITROGEN, %	1.26		1953		148	
REID VAPOR PRESSURE. N/M^2 (PSI)			1724 (0.25)		1379 (0.20)	
FLASH POINT, °K (°F)			284 (52)		283 (50)	
DISTILLATION	D-86		GC (SIMULATED TBP)		GC	
	°K	(°F)	°K	(°F)	°K	(°F)
IBP	361	(190)	332	(139)	332	(138)
5%	400	(261)	370	(206)	369	(204)
10	412	(282)	393	(248)	392	(247)
15	423	(302)	406	(272)	405	(269)
20	432	(318)	417	(291)	415	(287)
30	450	(350)	437	(328)	434	(322)
40	470	(387)	459	(367)	454	(357)
50	495	(432)	486	(415)	479	(402)
60	518	(473)	506	(452)	500	(440)
70	539	(511)	526	(488)	521	(478)
80	560	(548)	552	(534)	543	(518)
90	582	(589)	584	(591)	575	(575)
EP	597	(615)	621	(658)	620	(656)

FIGURE 2

SHALE OIL HYDROTREATING

311–616°K (100–650°F) Fraction

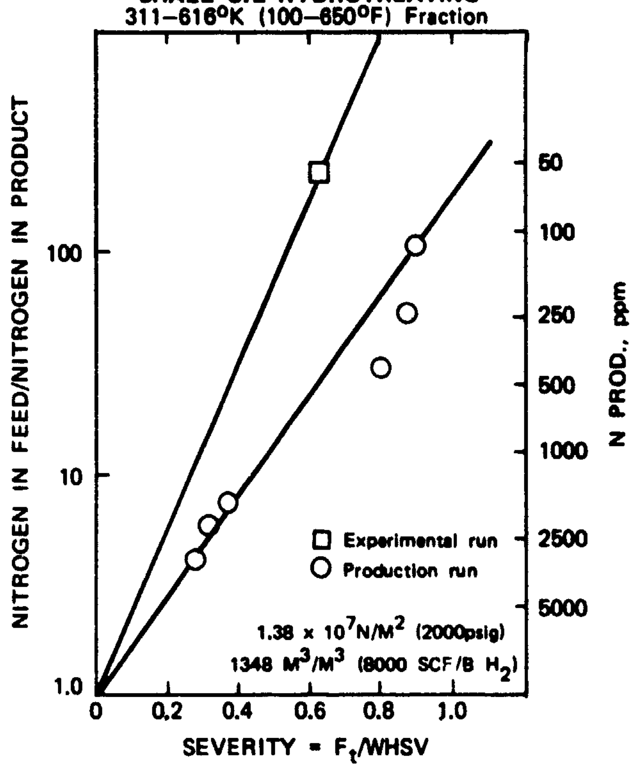
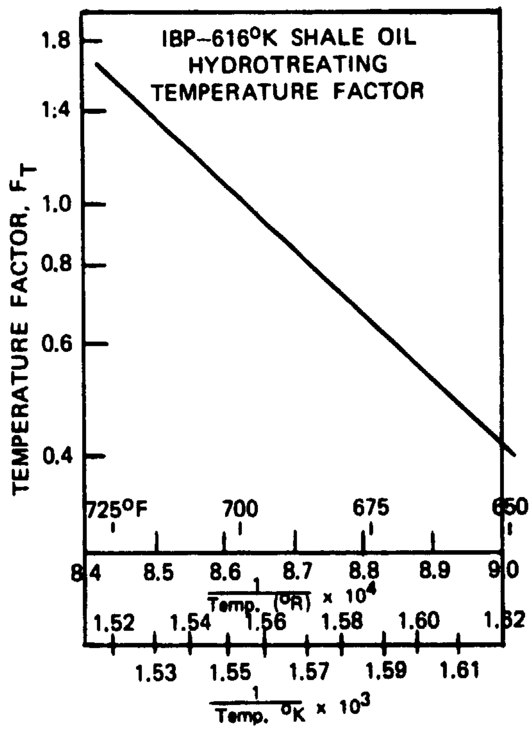


FIGURE 3



to a required temperature increase of 15^{o}K (27^{o}F) to double the reaction rate. This value for the activation energy is substantially higher than that observed for the 311-616^{o}K (100-650^{o}F) fraction of 1.07 x 10^8 joule/Kg mole (25.6 kcal/gm mole), which is a more usual value for this reaction. This, together with the curvature in the correlation line in Figure 4, which indicates a deviation from first order kinetics, suggests some poisoning effect of the NH_3 produced in this reaction. Additional work would be required to confirm this, however.

A standard catalyst activity check on a mid-continent fluid catalytic light cycle oil which was run before and after the experimental program on the shale oil indicated no detectable catalyst deactivation during the course of this run. In Figure 4, therefore, a value of 1.0 has been assigned to the parameter "catalyst activity" for the data points from this run. The initial activity observed in the production run was somewhat lower, however, as is shown in Figure 6 by the value of 0.8 for catalyst activity at the beginning of the run. Catalyst activity continued to decline during the run, probably as a result of the high operating temperature (676^{o}K - 755^{o}F). The rate of catalyst deactivation, as shown in Figure 6, would require a rate of temperature increase of 3-4^{o}K (5-6^{o}F)/week to maintain a constant level of denitrogenation. The values for catalyst activity used to calculate the severity factor for the data points from the production run in Figure 4 are obtained from Figure 6. Analyses of the 616-783^{o}K (650-950^{o}F) raw shale oil fraction and the composite product from the production run are shown in Table IV. Hydrogen consumption during the production run was 329 m^3/m^3 (1950 SCF/B).

2. Hydrocracking of the Denitrogenated 616-783^{o}K (650-950^{o}F) Shale Oil Fraction

The initial tests in the hydrotreating zone to determine required conditions gave the following results:

Temperature, ^{o}K (^{o}F)	625 (665)	639 (690)	652 (715)
Ppm N in Product	82	29	21
Conversion to 311^{o}K (100^{o}F) and Lighter	-----------------	nil	---------------

These results indicate a significant reduction in the rate of denitrogenation as nitrogen removal approaches 99.9% of the feed nitrogen. This effect is commonly seen in HDN processing at high conversions.

TABLE IV

SHALE OIL 616-783°K (650-950°F) HYDROTREATING PRODUCTION RUN

	FEEDSTOCK		COMPOSITE PRODUCT	
SAMPLE NO.	D3648		33287	
GRAVITY, Kg/M^3 (°API)	958.6 (16.1)		864.4 (32.2)	
% SULFUR	0.563		0.002	
% HYDROGEN	11.00		13.41	
% NITROGEN	2.23		233 (PPM)	
DISTILLATION	ASTM D1160		G.C. DIST.	
	°K	°F	°K	°F
IBP	544	519	395	252
5%	643	698	466	379
10	652	714	505	450
20	660	729	557	544
30	671	749	596	614
40	685	774	627	669
50	700	800	648	707
60	716	829	669	745
70	731	856	692	786
80	747	885	714	825
90	770	927	746	883
95	786	956	771	928
EP	–	–	816	1010

FIGURE 4

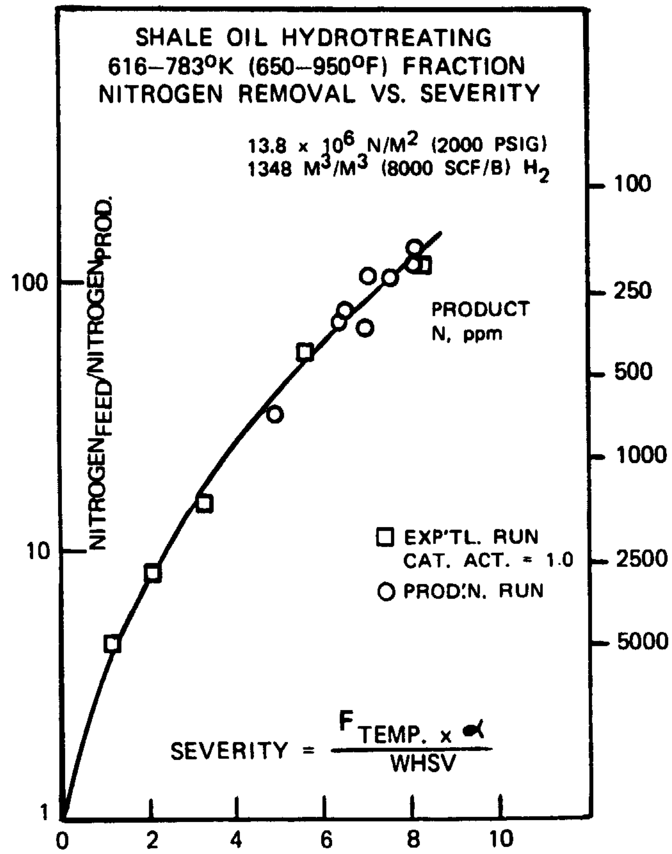


FIGURE 5

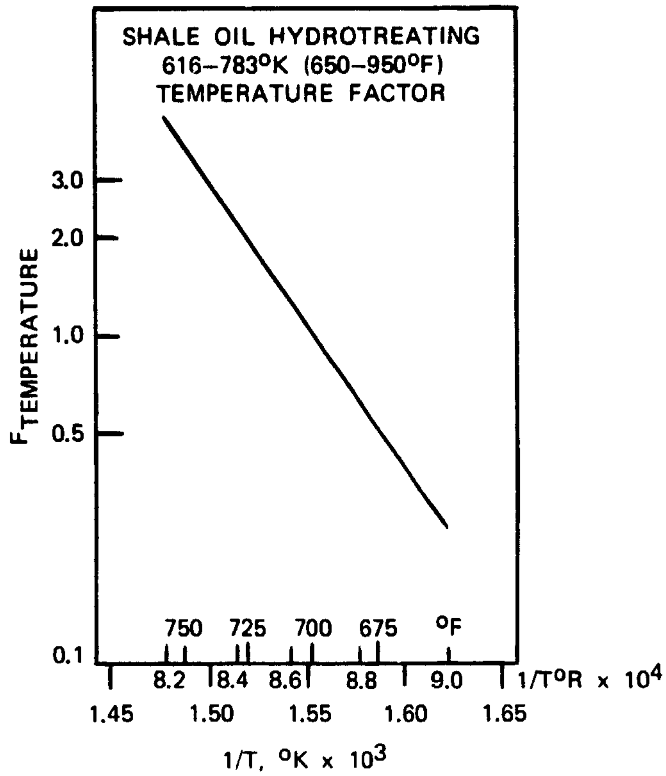


FIGURE 6

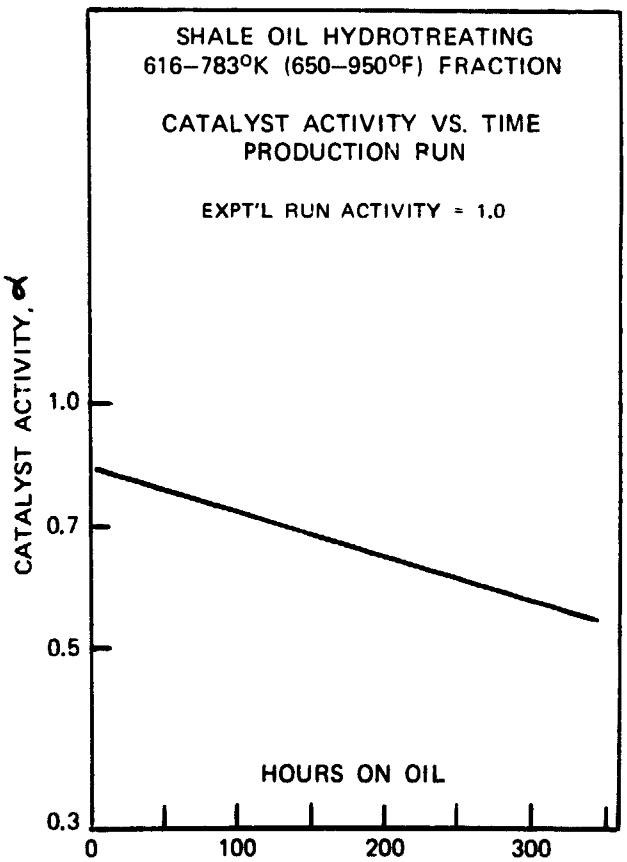


Table V shows the data for the weight balanced yield tests made during the hydrocracking production run and also the preliminary process variable run. Since both temperature and catalyst activity were changing during the production run, an unambiguous kinetic analysis of the data is not possible. However, if first order kinetics (Figure 7) and an activation energy of 2.5×10^8 Joule/Kg mole (60 kcal/gm. mole) (Figure 8) are assumed (based on petroleum gas oil hydrocracking data), catalyst activity as a function of time can be calculated, which is shown in Figure 9. Although this plot indicates a decline in catalyst activity by two orders of magnitude, this is a loss of initial "flush" activity, and does not appear to be entirely unreasonable for the first 200 hours of operation based on past experience with this catalyst system.

In Figure 10, the yield of the 422-561^{o}K (300-550^{o}F) fraction as a wt. % of feed is plotted as a function of conversion to 616^{o}K (650^{o}F) and lighter. A maximum 422-561^{o}K (300-550^{o}F) yield appears at approximately 70% conversion. Figure 11 is a plot of the 311-616^{o}K (100-650^{o}F) yield on feed, again as a function of conversion to 616^{o}K (650^{o}F) and lighter. The yield of this fraction increases with conversion over the entire range, but not linearly. As conversion increases, losses to 311^{o}K (100^{o}F)- also increase. H_2 consumption as a function of conversion to 616^{o}K (650^{o}F)$^{-}$, as shown in Figure 12, ranges from 51 to 135 m^3/m^3 (300-800 SCF/B). These yields are based on the data obtained after 50 hours on oil when the conversion level was in a normal range.

The product from the production run was composited to make a liquid product of 797.2 Kg/m^3 (46.0 ^{o}API) gravity, in a yield of 81.08% by weight and 87.90% by volume. The boiling point distribution of 311^{o}K (100^{o}F)+ liquid product as weight percent yield on hydrocracker feed is shown in Figure 13. The yield of 311-616^{o}K (100-650^{o}F) fraction was 52.7 wt. % of the feed.

These yields are unusually low due to the excessive cracking to 311^{o}K (100^{o}F)$^{-}$ products during the first two days of the run. If catalyst activity had been stabilized and conversion held at 70% to 616^{o}K (650^{o}F)$^{-}$, the liquid product yield would have been 95.8 wt. % or 103.9 vol. %. Yield of 100-650^{o}F fraction would have been 65.8 wt. % on feed, as shown in Figure 11.

TABLE V

616-783°K (650-950°F) SHALE OIL HYDROCRACKING
13.8×10^6 N/M^2 (2000 PSIG), 1685 M^3/M^3 (10,000 SCF/B) H_2

	EXPTL. RUN		PRODUCTION RUN						
TEST NO.	1	2	1	2	3	4	5	6	7
HOURS ON OIL	–	–	50	77	100	106	130	154	188
TEMP									
HDN °K	639	639	639	639	639	639	639	639	639
HDN °F	690	690	690	690	690	690	690	690	690
HCK °K	631	616	551	577	589	595	606	615	623
HCK °F	676	650	533	580	600	612	632	648	662
WHSV									
HDN REACTOR	1.01	0.99	1.03	1.03	1.01	1.01	1.00	1.03	1.01
HCK REACTOR	1.01	0.99	0.77	0.77	0.76	0.76	0.75	0.77	0.76
YIELDS, WT. % ON FEED									
C_3-	2.61	0.57	0.37	0.21	0.15	0.18	0.33	0.64	0.76
C_4	13.14	2.94	1.41	0.27	0.49	0.74	1.90	4.29	4.72
C_5	11.75	2.77	1.30	0.19	0.56	0.78	2.01	4.52	4.78
310-422°K (100-300°F)	14.24	20.93	10.04	3.00	6.75	8.36	18.93	32.92	33.14
422-472°K (300-390°F)	56.93	15.06	8.39	5.24	7.46	8.44	13.88	15.07	15.85
472-561°K (390-550°F)	3.43	22.84	17.88	18.87	20.56	20.94	21.95	15.60	15.11
561-616°K (550-650°F)	0	9.16	12.27	17.04	14.40	13.77	10.38	6.82	5.72
616+°K (650+°F)	0	26.80	48.92	55.73	50.17	47.45	31.56	21.47	21.26
H_2 CONS., WT. %	2.13	1.09	0.60	0.58	0.58	0.68	0.95	1.37	1.38

FIGURE 7

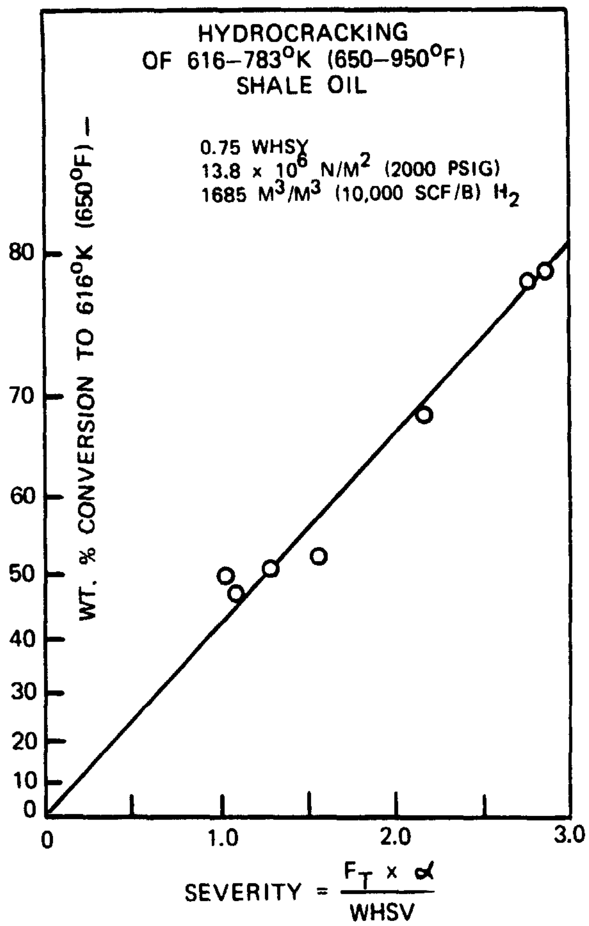


FIGURE 8

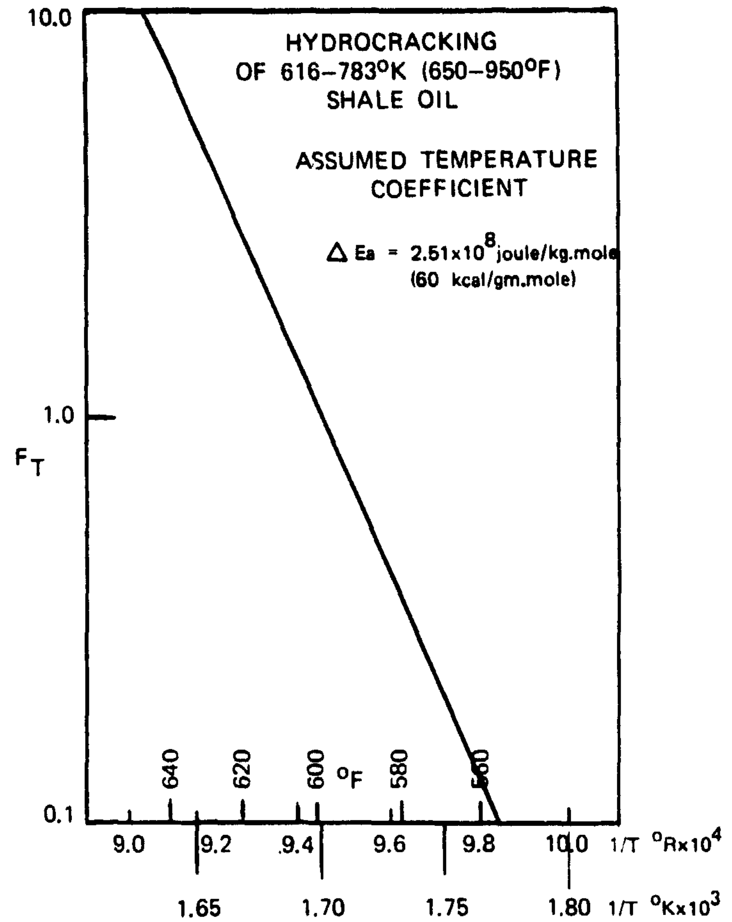


FIGURE 9

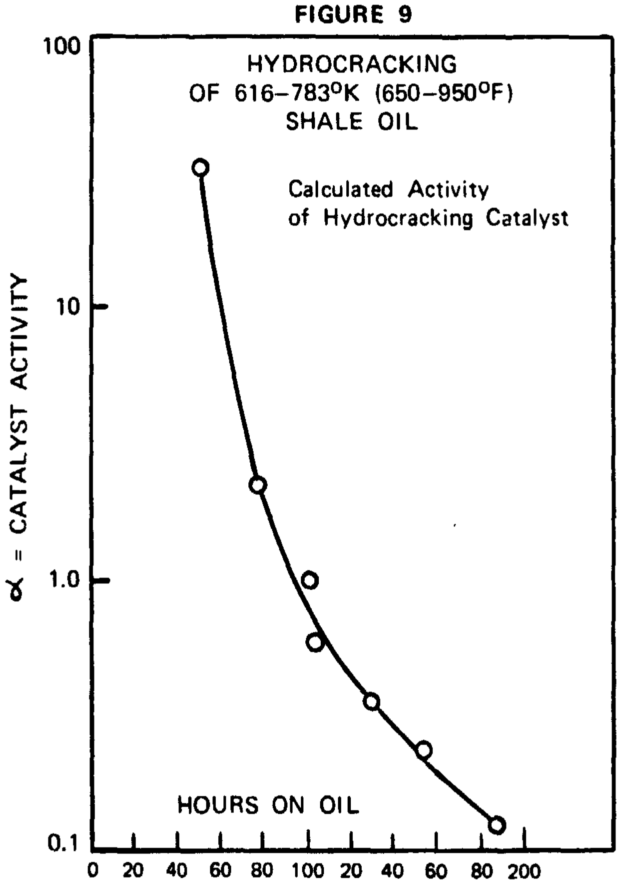


FIGURE 10

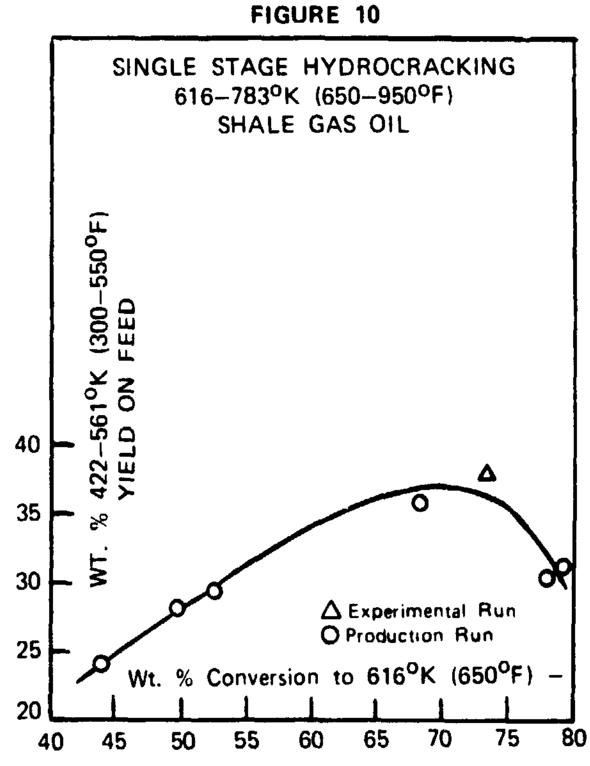


FIGURE 11

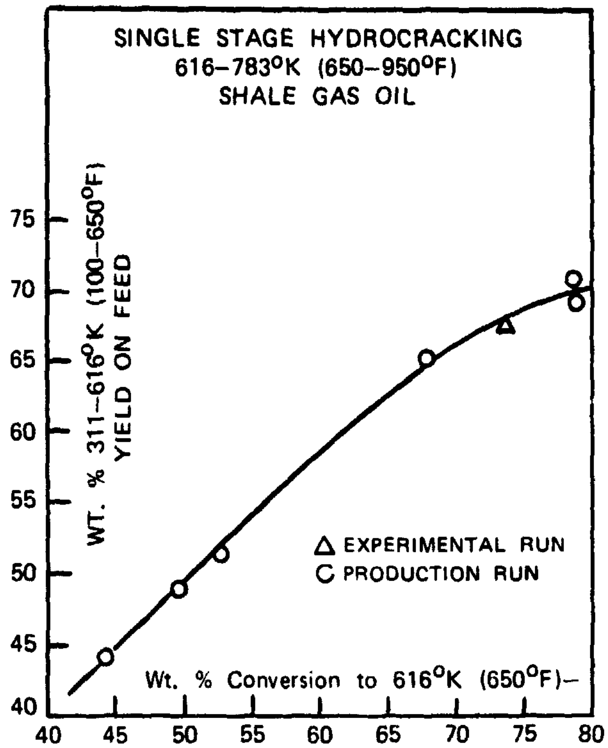


FIGURE 13

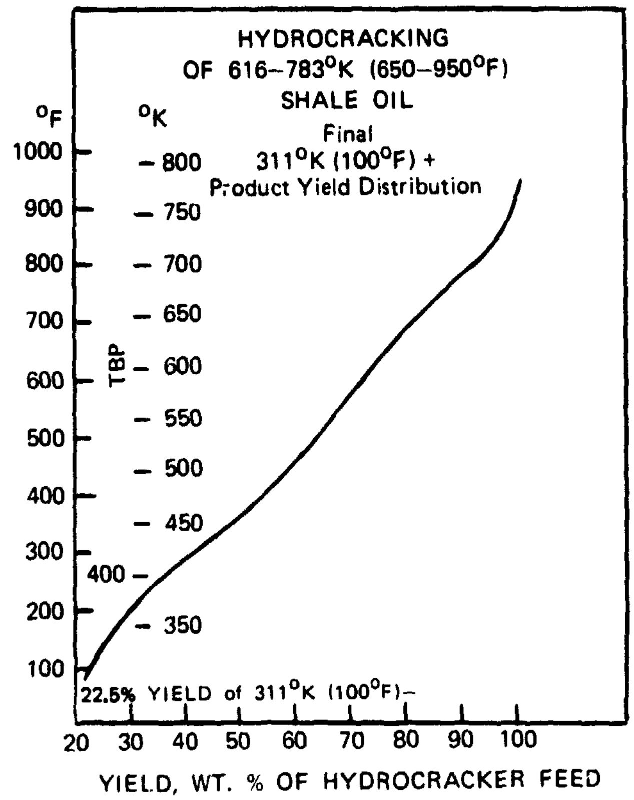
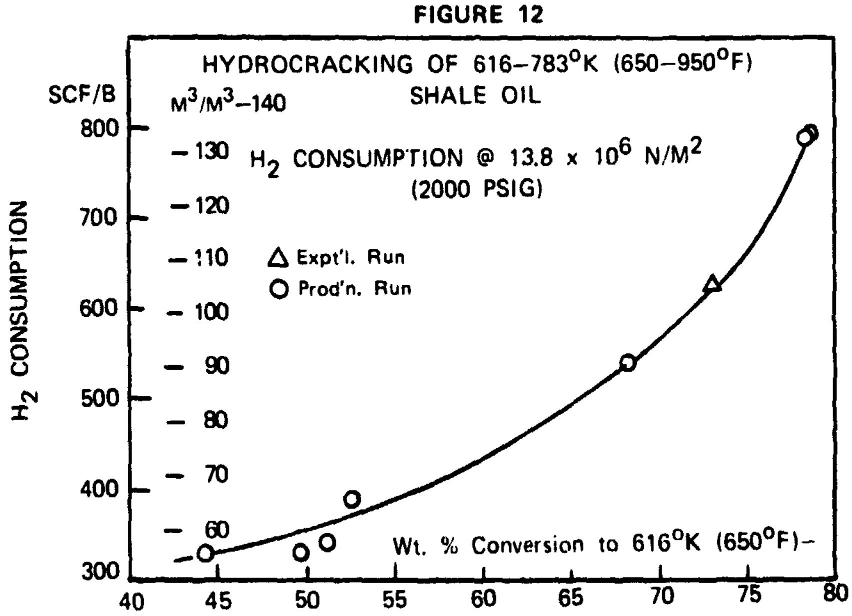


FIGURE 12



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3. Final Product Yields and Analyses

The blending and fractionations to produce the final products were based on the wt. % yields on the original shale oil charge actually obtained. As noted in the previous section, however, the yields obtained from the hydrocracking operation were abnormally low due to excessive cracking during the initial part of the run. The yields actually obtained are shown in the following table, and the corrections for the low hydrocracking yield are noted.

Wt. % Yield on Full Range Shale Oil

SAMPLE	LOW SEVERITY				HIGH SEVERITY			
Boiling Range, °K , °F	311-616 100-650	394-616 250-650	311-561 100-550	394-561 250-550	311-616 100-650	394-616 250-650	311-561 100-550	394-561 250-550
LOW YIELD SAMPLES, NO.	33315	33316	33318	33317	33340	33341	33343	33342
311-422°K (100-300°F)	7.82	3.81	7.82	3.81	8.28	4.58	8.28	4.58
422-561°K (300-550°F)	21.09	21.09	21.09	21.09	21.61	21.61	21.61	21.61
561-616°K (550-650°F)	6.01	6.01	-	-	5.03	5.03	-	-
TOTAL	34.92	30.91	28.91	24.90	34.92	31.22	29.89	26.19
HIGH YIELD SAMPLES, NO.	33365	33366	33368	33367	33408	33409	33411	33410
311-422°K (100-300°F)	13.62*	5.44	13.62	5.44	14.08	5.78	14.08	5.78
422-561°K (300-550°F)	29.11	29.11	29.11	29.11	29.64	29.64	29.64	29.64
561-616°K (550-650°F)	8.47	8.47	-	-	7.49	7.49	-	-
TOTAL	51.20	43.02	42.73	34.55	51.20	42.91	43.72	35.42

*If the hydrocracking operation had been carried out entirely with normal catalyst activity and at 70% conversion to 616°K⁻, the high yield values for the 311-616°K range samples would have been 14.92% 311-422, 30.57% 422-561, and 9.63% 561-616°K; a total of 55.12% on shale oil.

Analyses of all the final product samples are given in Table VI.

TABLE VI (p. 1)

SHALE SYNCRUDE PRODUCT DISTILLATIONS (ASTM D-86)

LOW YIELD PRODUCTS

SAMPLE NO.	33315		33316		33317		33318		33340		33341		33342		33343	
	°K	°F	°K	°F	°K	°F	°K	°F	°K	°F	°K	°F	°K	°F	°K	°F
IBP	372	211	425	305	425	305	374	213	377	219	424	303	424	304	380	224
5%	402	264	436	325	435	324	400	261	404	267	436	326	434	322	405	269
10	412	283	441	334	438	329	408	275	414	285	439	330	436	326	410	279
15	419	295	444	340	443	338	412	283	423	302	446	343	441	335	419	295
20	430	314	451	353	445	341	423	302	431	316	450	351	447	345	426	308
30	445	342	463	374	450	351	437	327	445	342	462	372	454	358	[illegible]	332
40	465	377	480	404	464	375	449	349	465	377	477	400	466	379	[illegible]	[illegible]
50	486	415	498	437	476	397	466	379	482	409	495	431	478	401	[illegible]	[illegible]
60	505	450	515	468	489	421	482	408	502	445	511	461	491	425	[illegible]	[illegible]
70	525	485	532	499	502	445	497	435	521	478	529	493	504	448	499	438
80	545	522	551	532	514	465	511	460	542	516	548	527	516	469	512	462
90	574	573	576	578	526	487	524	484	569	564	573	572	529	493	527	489
95	590	603	592	606	534	501	533	500	587	597	590	602	538	509	537	507
EP	594	610	596	613	543	518	545	521	594	610	596	613	550	531	554	537

HIGH YIELD PRODUCTS

SAMPLE NO.	33365		33366		33367		33368		33408		33409		33410		33411	
	°K	°F	°K	°F	°K	°F	°K	°F	°K	°F	°K	°F	°K	°F	°K	°F
IBP	349	168	422	301	423	302	350	170	352	175	424	304	425	306	369	204
5%	385	234	435	323	433	320	384	231	389	241	437	327	435	323	389	240
10	396	254	436	326	434	321	394	249	400	261	441	334	438	329	403	266
15	408	275	443	338	440	332	403	266	409	277	445	341	444	339	411	281
20	418	293	449	349	443	338	412	283	420	297	451	352	446	343	419	295
30	435	324	461	370	452	354	428	311	438	329	462	373	456	361	435	324
40	454	357	476	398	463	374	443	338	456	361	477	400	467	381	450	350
50	475	395	495	431	476	397	459	367	475	395	494	429	479	403	466	380
60	497	435	512	463	490	422	477	400	497	436	512	462	491	425	482	409
70	519	474	531	496	504	447	494	429	519	474	530	494	504	448	497	436
80	541	515	550	531	516	469	510	458	541	514	549	528	516	470	512	463
90	569	564	575	575	530	494	526	488	568	563	573	572	530	495	528	491
95	586	595	590	602	539	510	537	507	585	594	587	598	540	512	539	511
EP	591	605	593	608	550	530	549	528	592	607	594	609	552	535	552	534

TABLE VI (p. 2)

FINAL PRODUCT ANALYSES

	LOW YIELD SHALE PRODUCTS								HIGH YIELD SHALE PRODUCTS							
	LOW SEVERITY				HIGH SEVERITY				LOW SEVERITY				HIGH SEVERITY			
BOILING RANGE °K	IBP-616	394-616	394-561	IBP-561	IBP-616	394-616	394-561	IBP-561	IBP-616	394-616	394-561	IBP-561	IBP-616	394-616	394-561	IBP-561
°F	(IBP-650)	(250-650)	(250-550)	(IBP-550)	(IBP-650)	(250-650)	(250-550)	(IBP-550)	(IBP-650)	(250-650)	(250-550)	(IBP-550)	(IBP-650)	(250-650)	(250-550)	(IBP-550)
SAMPLE NUMBER	33315	33316	33317	33318	33340	33341	33342	33343	33365	33366	33367	33368	33408	33409	33410	33411
SPECIFIC GRAVITY KG/M^3	804.0	817.0	806.8	794.5	797.7	808.1	802.2	791.4	797.2	814.6	805.4	787.4	793.6	810.0	803.5	787.4
REID VAPOR PRESSURE N/M^2	1034	–	–	345	2758	–	–	1034	7585	–	–	6895	8619	–	–	7585
(PSI)	(0.15)	–	–	(0.05)	(0.40)	–	–	(0.15)	(1.10)	–	–	(1.00)	(1.25)	–	–	(1.10)
FLASH POINT, °K	–	315	311	–	–	312	312	–	–	314	312	–	–	312	309	–
(°F)	–	(108)	(100)	–	–	(102)	(102)	–	–	(106)	(102)	–	–	(102)	(96)	–
FREEZING POINT, °K		258	229	225	256	258	231	229	251	255	227	222	250	254	226	223
(°F)	0	(+5)	(–47)	(–54)	(+1)	(+5)	(–44)	(–47)	(–8)	(–1)	(–50)	(–58)	(–9)	(–3)	(–52)	(–58)
VISCOSITY @ 239°K (–30°F), CS	Solid	Solid	6.781	4.736	Solid	Solid	6.990	5.059	Solid	Solid	6.918	4.093	Solid	Solid	7.060	4.326
NET HEAT OF COMBUSTION																
(cal/g)	(10,477)	(10,433)	(10,545)	(10,428)	(10,545)	(10,482)	(10,466)	(10,499)	(10,565)	(10,531)	(10,596)	(10,622)	(10,595)	(10,488)	(10,532)	(10,605)
EXISTING GUM, mg	16.2(1)	51.4(1)	40.2(2)	32.2(2)	0.8(1)	19.2(1)	8.6(2)	9.0(2)	26.8(1)	61.8(1)	23.4(2)	17.0(2)	9.2(1)	32.8(1)	16.0(2)	15.6(2)
SMOKE POINT	21	20	21	22	26	26	24	26	23	20	22	25	26	25	25	27
AROMATICS, %	21.9	25.9	22.2	19.0	13.7	17.4	17.1	13.5	15.7	20.3	17.9	13.7	12.1	15.4	13.2	11.4
OLEFINS, %	1.1	0.8	1.1	1.0	0.8	1.0	1.2	0.9	0.8	0.9	1.3	0.8	0.6	1.0	1.0	0.8
NAPHTHALENES, %	1.0	1.2	0.5	0.5	0.4	0.4	0.2	0.2	0.75	0.93	0.42	0.33	0.3	0.35	0.21	0.17
HYDROGEN, %	13.64	13.66	13.68	13.73	13.82	13.86	13.95	13.76	13.82	13.37	13.80	13.70	13.98	13.95	13.95	13.98
NITROGEN, ppm	1954	2233	2011	1750	161	168	152	132	1305	1581	1397	1138	101	144	76	88
TOTAL SULFUR, ppm	9.8	14.1	5.6	6.0	9.0	3.0	1.0	2.0	14.0	12.0	6.0	5.0	10.8	4.8	1.5	1.7
MERCAPTANS, ppm	2	2	2	2	3	2	–	–	1	–	–	–	1	–	–	–
OXYGEN, %	0.03	0.05	0.06	0.04	0.03	0.05	0.09	0.09	0.08	0.14	0.14	0.13	0.11	0.10	0.07	0.10
THERMAL STABILITY	4+	4+	4+	1	–	4+	3	4+	4+	4+	4+	4	4+	4	4+	4+

(1) D-381 STEAM JET METHOD @ 506°K (450°F)
(2) D-381 AIR JET METHOD @ 428°K (311°F)

4. Additional Processing Options to Increase Jet Fuel Yields from Shale Oil

a. Hydrocracking the 616-783°K (650-950°F) Fraction to 100% Conversion to 616°K (650°F)- Products by Extinction Recycle

Based on data from extinction recycle hydrocracking of petroleum gas oils, in which the 616°K+ (650°F+) product would be recycled to the hydrocracker, the product distribution at 100% conversion to 616°K- (650°F-) is closely approximated by the product distribution of cracked products of once through conversion at the same conversion per pass. Based on this assumption, we calculate that the high yield products would be increased by the following amounts:

Fraction	Δ Yield, Wt. % on Shale Oil
311-422°K (100-300°F)	+2.47
394-422°K (250-300°F)	+0.98
422-561°K (300-550°F)	+4.83
561-616°K (550-650°F)	+1.35

b. Delayed Coking of the 783°K (950°F)+ Shale Oil Bottoms

In order to obtain the desired 40% yield of 422-561°K (300-550°F) material, some of the 783°K (950°F)+ fraction (34% of the shale oil) would have to be converted. One of the commonly proposed processes for upgrading of raw shale oil is delayed coking. One test run was made in a delayed coking pilot plant on the 783°K (950°F)+ raw shale bottoms. None of the product from this run was used to prepare any of the final product samples, but the data were used to calculate potential increased yields of jet fuel if this process were incorporated in the overall scheme.

Yields from the delayed coking run of the 783°K (950°F)+ raw shale are shown below.

Product	Wt. % on Feed	Kg/m^3	^{o}API
Gas	7.97	-	-
IBP-452^{o}K (IBP-355^{o}F)	10.25	749.5	57.3
452-527^{o}K (355-490^{o}F)	7.85	831.4	38.7
527-589^{o}K (490-600^{o}F)	8.27	885.4	28.3
589-755^{o}K (600-900^{o}F)	21.75	951.0	17.3
H_2S	0.07	-	-
Coke	43.84	-	-

The distillation curve of the 311-755^{o}K (100-900^{o}F) liquid product is shown in Figure 14.

The densities of the fractions of the product from the coking run are somewhat lower than those of the equivalent pyrolysis shale oil fractions. Based on this observation and other past experience, the processing characteristics and product yields and qualities were assumed to be about the same for the coker product and pyrolysis oil fractions of the same boiling range. On this basis, the following incremental yields have been calculated.

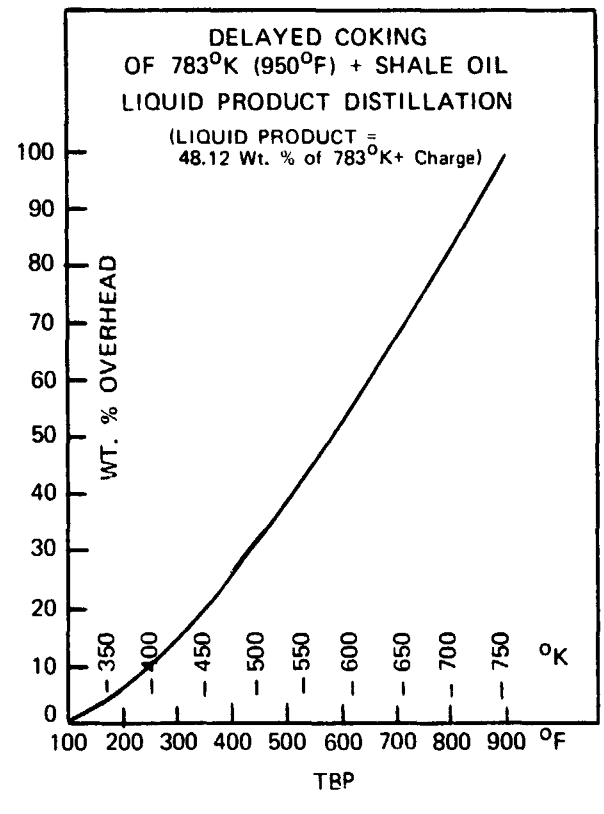
LOW YIELD PRODUCTS	
Fraction	Δ Yield, Wt. % on Shale Oil
311-422°K (100-300°F)	2.42
394-422°K (250-300°F)	1.19
422-561°K (300-550°F)	5.17
561-616°K (550-650°F)	2.34
HIGH YIELD PRODUCTS (Hydrocracking of 616-783°K Coker Gas Oil to 100% Conversion to 616°K-)	
311-422°K (100-300°F)	4.10
394-422°K (250-300°F)	2.25
422 -561°K (300-550°F)	8.43
561-615°K (550-650°F)	3.26

Maximum Yield Case

Using both of the above process alternates, i.e., coking of the 783°K+ shale oil bottoms and extinction recycle conversion of the 616-783°K shale and coker gas oils, the following maximum yields (average for high and lower severity HDN) should be attainable.

Fraction	Wt. % on Full Range Shale Oil	
	LOW YIELD	HIGH YIELD
311-422°K (100-300°F)	10.5	21.5
394-422°K (250-300°F)	4.2	11.2
422-561°K (300-550°F)	26.5	43.8
561-616°K (550-650°F)	7.9	14.2
311-616°K (100-650°F)	44.9	79.5

FIGURE 14


DELAYED COKING
OF 783°K (950°F) + SHALE OIL
LIQUID PRODUCT DISTILLATION
(LIQUID PRODUCT =
48.12 Wt. % of 783°K+ Charge)
WT. % OVERHEAD
100
90
80
70
60
50
40
30
20
10
0
350
400
450
500
550
600
650
700
750
°K
100
200
300
400
500
600
700
800
900
°F
TBP

IV. COAL SYNCRUDES

A. Experimental Procedure

1. Feedstock Preparation and Analysis

In the coal syncrude phase of the program, it was found necessary to use two feedstocks, prepared by the H-COAL and COED processes. Originally it was planned to use the H-Coal syncrude exclusively, but the only sample was not available in sufficient quantity to prepare all the required samples. It was also a low conversion sample, containing 39% 616°K (650°F) and lighter material, essentially no 616-700°K (650-800°F), and the balance 700°K (800°F)+ vacuum bottoms. This latter material was a solid, low hydrogen content material containing 14.6% ash, and any attempt to process it was considered impractical. For this reason, the H-Coal 616°K (650°F)⁻ syncrude was chosen to produce the low yield samples only. The only other coal syncrude readily available was a COED product, and a sufficient quantity of this material was obtained to produce the high yield products.

a. H-Coal

The H-Coal sample obtained was derived from Illinois #6 Coal, prepared in the HRI PDU at ∿3.1 Kg coal/hr.m^3 reactor volume (∿50 lbs. coal/hr. ft^3). This is a severity intermediate between normal syncrude and fuel oil operations. The overhead (616°K-) and bottoms fractions (700°K+) were received separately. The overhead fraction was fractionated on a laboratory column into IBP-422, 422-561, 561-616 and 616°K+ (IBP-300, 300-550, 550-650 and 650°F+) cuts. The analyses of the total overhead, the distillation cuts and the vacuum bottoms as received are given in Table VII. The distillation curve of the overhead is shown in Figure 15. The total overhead liquid as received was used as feedstock to the hydrotreating step.

b. COED

485 Kg (1070 Lbs.) of COED syncrude (derived from Utah Coal) were charged to the .203 m (8") batch fractionator, used earlier on the shale oil runs. Overhead was taken until overhead temperature indicated a 616°K (650°F) cut point.

Water was not present as a separate phase in the charge stock, but approximately 16 wt. % water was separated by decanting from the overhead fractions. Recovery was only 92 wt. %, but since water was found in the traps of the vacuum system it is likely that the 8% loss also represents water.

The water apparently gave false indications of temperatures, and the bottoms from the .203 m (8") still had an initial boiling point of approximately 561°K (550°F). These were run on the .102 m (4") still to a 700°K (800°F) cut point. Yields based on a water free total syncrude charge are plotted against temperature in Figure 16.

All 561-700°K (550-800°F) product from the .102 m (4") still was composited as the feedstock to the hydrocracking step. The IBP-561°K (550°F) fractions were composited and filtered thru supercell to remove any remaining water. This stock was used as the feedstock to the hydrotreater.

Because of the water present in the initial fractionation of the COED oil, an IBP-422°K (300°F) fraction was not obtained for analysis. A small portion of the first two fractions from that run were blended proportional to yield and rerun in a .051 m (2") Oldershaw still.

Analyses of the syncrude and fractions are given in Table VIII. A completely dried sample of the syncrude could not be prepared, so some of the values for the syncrude had to be calculated from the analyses of the fractions.

2. Hydrotreating of Coal Syncrudes

a. H-Coal Syncrude Hydrotreating

In the case of coal syncrude, processing to meet the hydrogen content specification was found to be the limiting factor. Therefore, product hydrogen was used to monitor product quality and to determine when adjustments in operating conditions were needed to maintain suitable quality.

TABLE VII

H–COAL COMPOSITE FEED AND FRACTIONS

	FEED	IBP-422°K IBP-300°F	422-561°K 300-550	561-616°K 550-650	616+°K 650+	VACUUM BOTTOMS
GRAVITY, Kg/M^3 (°API)	870.8	778.4	890.0	969.2	1033.6	–
	(31.0)	(50.3)	(27.5)	(14.5)	(5.4)	–
% HYDROGEN	11.8	13.3	11.2	10.0	9.0	5.75
% CARBON	87.1	86.6	87.2	89.2	89.2	74.39
% SULFUR	0.170	0.129	0.073	0.110	0.199	1.93
NITROGEN, ppm	1722	659	1749	1651	5044	1.16%
% OXYGEN	0.48	0.61	1.00	0.49	1.34	4.60
% ASH	0.0	–	–	–	–	14.62
POUR POINT, °K (°F)	<211					
	(<-80)					
RING & BALL						
SOFTENING PT. °K (°F)						390
						(243)
KINEMATIC VISCOSITY, cs						
@ 255°K (0°F)	4.658	1.373	5.749			
@ 311°K (100°F)	1.343		1.532	7.313	137.5	
@ 372°K (210°F)				1.887	7.50	
% OF TOTAL LIQUID	100	25	61.4	8.1	5.2	–
% OF TOTAL SYNCRUDE	28.44	7.11	17.46	2.30	1.48	71.56
% OF TOTAL SYNCRUDE, ASH FREE	38.91	9.73	23.89	3.15	2.02	61.09
% MONOAROMATICS		14.1	44.9	29.2	10.6	
% POLYCYCLIC AROMATICS		0	6.4	42.2	52.7	

TABLE VIII

COED OIL COMPOSITE FEED AND FRACTIONS

	FEED	IBP-422°K (IBP-300°F)	422-561 (300-550)	561-616 (550-650)	616-700 (650-800)	700+ (800+)
GRAVITY, Kg/M^3 (°API)	945.2	789.2	903.0	946.5	956.0	1002.8
	(18.2)	(47.8)	(25.2)	(18.0)	(16.5)	(9.6)
% HYDROGEN	10.94*	14.8	11.23	10.58	10.86	10.09
% CARBON	87.48	85.2	86.45	87.9	88.10	87.54
% SULFUR	.023*	.027	.021	.016	.032	<0.02
NITROGEN, ppm	3853	677	3696	3726	3399	4285
% OXYGEN	.98*	0.34	1.31	0.86	0.74	1.02
% ASH	0.05	–	–	<0.001	<0.02	0.03
POUR POINT °K (°F)	300 (80)					
KINEMATIC VISCOSITY, CS						
@ 255°K (0°F)	–	1.449	12.42	–	–	
@ 311°K (100°F)	11.81	–	2.228	9.128	41.06	
@ 372°K (210°F)	–	–	–	2.092	4.860	
SAYBOLT VISCOSITY @ 372°K (210°F), CS						17.7
% RESINS		–	–	9.0	9.1	21.8
% MONO AROMATICS		16.2	51.0	34.4	20.0	14.1
% POLYAROMATICS		0.0	8.1	25.1	37.4	34.8
% OF TOTAL	100	4.0	32.5	18.0	27.0	18.5

*Back Calculated from Analyses of Fractions

FIGURE 15

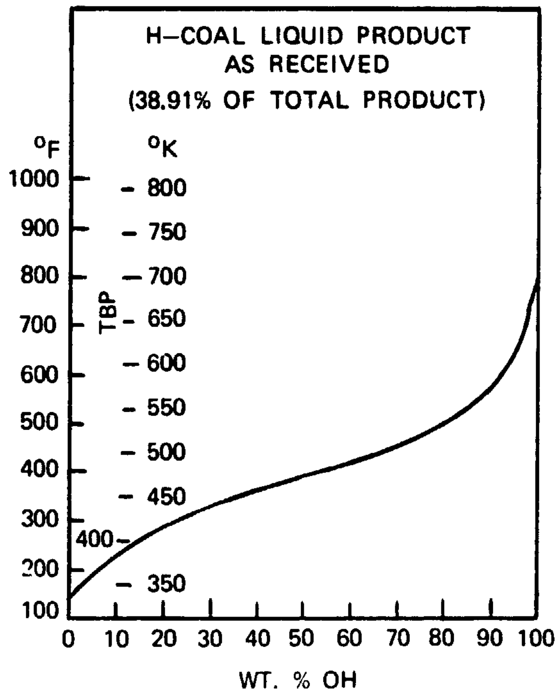
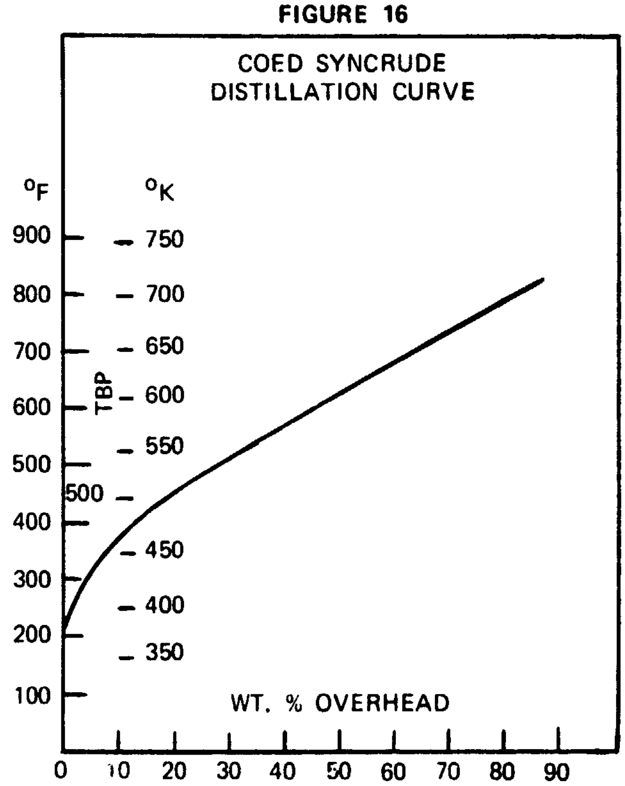


FIGURE 16



A short preliminary run was made to determine what processing conditions would be required to hydrotreat the H-Coal feed to the specified 12.75 and 13.5 percent product hydrogen levels. A .100 Kg charge of HDS-3A catalyst was diluted on a gradient with tabular alumina to help control temperature increases resulting from exothermic hydrogenation reactions, particularly aromatic saturation. The mixture ranged from 3 parts of alumina for each part of catalyst at the inlet of the bed to a ratio of 1.8 at the outlet. The following matrix of conditions was selected for investigation during the experimental run:

Temperature, ^{o}K (^{o}F)	616-644 (650-700)
Pressure, N/m^2 (PSIG)	13.8-17.2 x 10^6 (2000-2500)
WHSV, hr^{-1}	0.33-1.0
H_2 Rate, m^3/m^3 (SCF/B)	1348 (8000)

The hydrotreating production run on the H-Coal feed was made using a .500 Kg charge of HDS-3A catalyst that was diluted with alumina on the same distribution gradient used for the preliminary run. The high hydrogen product run was made first to take advantage of fresh catalyst activity. Based on the results of the experimental run, the high severity portion of the run was initiated at the following set of conditions:

Temperature, ^{o}K (^{o}F)	630 (675)
Pressure, N/m^2 (PSIG)	17.2 x 10^6 (2500)
WHSV, hr^{-1}	0.5
H_2 Rate, m^3/m^3 (SCF/B)	1348 (8000)

By the end of this segment of the run, temperature had been increased to 636^{o}K (685^{o}F) and WHSV had been reduced to 0.45 hr^{-1} in order to maintain required product quality. The low severity hydrogenation followed immediately on the same catalyst charge. Operating conditions for this portion of the run were set at:

Temperature, ^{o}K (^{o}F)	611 (640)
Pressure, N/m^2 (PSIG)	13.8×10^6 (2000)
WHSV, hr^{-1}	0.5
H_2 Rate, m^3/m^3 (SCF/B)	1348 (8000)

Approximately .038 m^3 (ten gallons) of feed were treated at each severity level.

b. IBP-561^{o}K (550^{o}F) COED Syncrude Hydrotreating

The IBP-561^{o}K (550^{o}F) fraction of COED Syncrude was hydrogenated at high and low severity conditions prior to blending with hydrocracked product to produce the high yield coal syncrude jet fuel samples. Feed inspections are presented in Table X.

Preparatory to the production run, a short experimental program was conducted to determine what operating conditions would be necessary to make the desired products. As with the H-Coal feed, hydrogen content is the limiting factor in meeting required product quality levels. The preliminary tests were made in a one inch diameter isothermal reactor over a .100 Kg charge of catalyst. To aid in controlling temperature increases resulting from the exothermic hydrogenation reactions, the .0016 m (1/16") catalyst was diluted on a gradient, with 3 parts tabular alumina to 1 part catalyst at the top of the bed ranging to a 1:8 ratio at the outlet. Process conditions selected for this investigation included:

Temperature, ^{o}K (^{o}F)	616,630,644 (650,675,700)
Pressure, N/m^2 (psig)	13.8×10^6 (2000)
WHSV, g. feed/hr./g. catalyst	0.5, 1.0
H_2 Rate, m^3/m^3 (SCF/B)	1348 (8000)

The hydrotreating production run on IBP-561°K (550°F) COED oil was conducted using .500 Kg of catalyst in a .051 m (two inch) diameter isothermal reactor. The catalyst was diluted on the same distribution gradient used for the experimental run. The high severity samples were produced first to take advantage of fresh catalyst activity. The initial conditions:

Temperature, °K (°F)	641 (695)
Pressure, N/m^2 (PSIG)	13.8×10^6 (2000)
WHSV, hr^{-1}	0.5
H_2 Rate, m^3/m^3 (SCF/B)	1348 (8000)

were selected on the basis of the results of the experimental run. Initially, catalyst activity was slightly higher than that observed during the experimental run, but activity declined at an average rate of 11% per day (on a relative WHSV basis) during the high severity operation. To compensate, it was necessary to increase reactor temperature to 647°K (705°F) by the end of this portion of the program. Low severity treating to produce the 12.75 percent hydrogen product followed immediately on the same catalyst charge. Conditions were set at:

Temperature, °K (°F)	616 (650)
Pressure, N/m^2 (psig)	13.8×10^6 (2000)
WHSV, hr^{-1}	0.8
H_2 Rate, m^3/m^3 (SCF/B)	1348 (8000)

Due to the extent of catalyst deactivation, an increase in temperature to 622°K (660°F) and a reduction in WHSV to 0.7 hr^{-1} was required before specification quality product was obtained. Catalyst activity decline continued during the low severity program at a rate of 8% per day, requiring a further reduction in WHSV to 0.65 hr^{-1} by the end of the run.

Approximately .042 m^3 (11 gallons) of feed were treated at each of the severity levels.

c. Hydrotreating of 561-700°K (550-800°F) COED Syncrude

In order to prevent deactivation of the catalyst during the hydrocracking step, hydrodenitrogenation of the 561-700°K (550-800°F) COED oil fraction was required. Previous work on similar heavy COED oil fractions indicated difficulty in achieving the product nitrogen levels of 200-400 ppm which were desired in this step. Therefore, no experimental tests were made, but the production run on this material was initiated directly at relatively severe conditions. Using .700 Kg of HDS-3A catalyst, the process conditions of 658°K (725°F), 0.75 WHSV (.525 Kg/hr. feed rate), 13.8 x 10^6 N/m^2 (2000 PSIG) and 1348 m^3/m^3 (8000 SCF/B) hydrogen rate which were selected resulted in a product nitrogen level of 175-200 ppm. This run was terminated after approximately four days, however, due to reactor plugging. The cause of this plugging was found to be a white solid material which deposited in the exit line from the reactor. After plugging again occurred on a second catalyst charge, the run was restarted with precautions taken to thoroughly dry the feedstock and relieve the restricted area in the reactor exit line. Plugging again occurred, but the run was completed after freeing the reactor exit of solids. The activity of the catalyst samples used to complete the run was somewhat lower than the activity noted during the first four days of the run. Therefore, in order to achieve the proper product nitrogen level, it was necessary to raise the temperature to 664°K (735°F) and lower the WHSV to 0.70.

A total of .132 m^3 (35 gallons) of hydrotreated 561-700°K (550-800°F) COED oil product was obtained from this run. Feed analyses are shown in Table XI.

3. Hydrocracking of the 561-700°K (550-800°F) Fraction of COED Syncrude

The hydrocracking portion of the study to prepare the high yield coal syncrude samples was performed in a single stage unit. This consisted of two reactors in series. The first reactor denitrogenates the feed to a level that is suitable for the second reactor, which is the hydrocracker. The total effluent from the first reactor is passed directly to the second where the hydrocracking reactions take place. Both catalysts are proprietary and are commercially available under license.

Preliminary experimental work was necessary to determine the conditions needed for the hydrocracking production run. Correlations from the first pass hydrotreating data were used to estimate the hydrotreating reactor conditions required to reduce the 237 ppm N feed to ∿20 ppm. The conditions for the production run were set at the following values:

1.05 WHSV (.300 Kg/hr.)

644^{o}K (700^{o}F)

1685 m^3 H_2/m^3 (10,000 SCF H_2/BBL)

13.8 x 10^6 N/m^2 (2000 PSIG)

These conditions produced an organic nitrogen content in the product of 22 ppm.

Two tests of the hydrocracking zone were performed in order to determine the process conditions for the production run. The test conditions are shown below:

Test No.	1	2
Pressure, N/m^2 (PSIG)	13.8 x 10^6 (2000)------	
WHSV	1.0--------------------	
Hydrogen Flow, m^3/m^3 (SCF/B)	1685 (10,000)----------	
Temperature, ^{o}K (^{o}F)	619 (654)	607 (634)

Based on these tests the process conditions chosen for the production run were 13.8 x 10^6 N/m^2 (2000 PSIG), 1.0 WHSV, 1685 m^3/m^3 (10,000 SCF/B) H_2 and 607^{o}K (634^{o}F) for 97% conversion to 616^{o}K (650^{o}F) and lighter.

The production run was performed using .051 m (2") I.D. reactors: the hydrodenitrogenation reactor contained .284 Kg of catalyst and the hydrocracking reactor contained .300 Kg. Both were diluted with inert tabular alumina in a linear manner to make up the required reactor volume (.001 m^3). The flush activity of the catalysts was removed by processing a medium boiling range gas oil over the catalyst for 72 hours before the production run. Tests of the first reactor effluent showed that the catalyst was not active, necessitating replacement. A new charge of the hydrodenitrogenation catalyst was installed and subsequent tests showed it had its normal activity.

The COED oil was then started over the catalyst. After a short lining out period, a sample of the second reactor effluent was taken. This sample showed that the second reactor catalyst had lost some of its activity due to the poor performance of the first charge of hydrotreating catalyst. The conversion to 616°K (650°F) and lighter had dropped from 97% to 79%, indicating an activity loss of 50% of its original value. However, the 79% conversion level was maintained. During the last quarter of the production run the feed rate was raised to .400 Kg/hr., with suitable corrections made in the reactor temperatures to maintain conversion. Corrections in the hydrocracking reactor temperature were also necessary during the course of the run to compensate for catalyst aging. Over the 330 hrs. of the production run the temperature was raised because of this aging by 23°K (42°F); other conditions remained constant (except for the WHSV change previously described). Approximately .117 m^3 (31 gals.) of feed were processed in this step.

4. Final Blending and Fractionation

The two 311-616°K (100-650°F) hydrotreated H-Coal products (i.e., high and low H content) were fractionated to produce the final samples in the same manner as described in Section III-A-4 for the shale oil products.

The hydrocracked 561-700°K (550-800°F) COED oil was fractionated into 311-616 (100-650) and 616°K (650°F)+ fractions. The 311-616°K (100-650°F) fraction was obtained in 70.2 wt. % yield on hydrocracker feed, or 27.0 wt. % yield on COED syncrude. Portions of this material were blended with the hydrotreated 311-561°K (100-550°F) COED products in a 45% hydrocrackate/55% 311-561°K (100-550°F) HDN product ratio to produce the high yield coal syncrude samples at two severity (H content) levels. These 311-616°K (100-650°F) composites were then fractionated as were the shale and H-Coal products to produce the final samples.

B. Results

1. Hydrotreating of Coal Syncrudes

a. H-Coal Syncrude Hydrotreating

Results from the experimental run were used to develop the relationship between product hydrogen content and operating severity shown in Figure 17. The effect of temperature on the hydrogenation reactions is presented in Arrhenius form in Figure 18. From this, an activity energy of 94 x 10^6 joule/Kg mole (22.5 kcal/g mol) was calculated. An increase in temperature of about 25°K (45°F) has an effect equivalent to doubling the reactor residence time. Differences in pressure also had an effect on the rate of hydrogenation and a factor has been included in the correlation to adjust for that (Figure 17).*

An important result of this run was the demonstration that the high hydrogen content specification of 13.5 percent could be attained at severe but practical operating conditions in a single pass operation. It had been anticipated that a two-stage process might be required to achieve the necessary level of hydrogenation.

As Figure 17 shows, there is a limiting value to hydrogen content of ~13.7 percent, and as it is approached, large increases in severity are required to make detectable gains in hydrogenation level. At the conditions employed, i.e., 616-644^{o}F (650-700^{o}F) and 13.8-17.2 x 10^6 N/m^2 (2000-2500 PSIG), the thermodynamics of bicyclic aromatics indicate about 99% conversion to the perhydro product at equilibrium. Therefore, this limiting value of 13.7% H is a stoichiometric rather than an equilibrium limit, and could not be increased by changing conditions (e.g., higher pressure).

Initial activity of the production run catalyst was about equal to that observed in the experimental run. Catalyst deactivation during the run, however, made necessary the increases in operating severity mentioned earlier. To compensate for loss of activity, an average severity increase equivalent to 1.7^{o}K (3.0^{o}F)/day during the high severity operation, and 1.1^{o}K (2.0^{o}F)/day at the low severity conditions was required.

The products from the high and low severity operations were each composited to form the total product samples. Inspections of the feed and product composites are presented in Table IX. Hydrogen consumption was calculated at about 185 m^3/m3 (1100 SCF/B) for the high severity tests and 108 m^3/m^3 (640 SCF/B) for the low severity operation.

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*$F_{P_{2000}} = \frac{WHSV(2000)}{WHSV(2500)}$ at constant conversion.

TABLE IX

FEED AND PRODUCT INSPECTIONS
H-COAL LIQUID COMPOSITE

	FEED	LOW SEVERITY PRODUCT		HIGH SEVERITY PRODUCT	
SAMPLE NO.	J-33276	J-33359		J-33361	
GRAVITY, Kg/M^3	870.8	849.3		833.8	
(°API)	(31.0)	(35.1)		(38.2)	
% HYDROGEN	11.81	12.75		13.60	
% SULFUR	0.170	0.0004		0.0006	
% NITROGEN	0.1722	0.0005		0	
% OXYGEN	0.63	0.11		0.04	
DISTILLATION BY GAS CHROMATOGRAPH					
IBP		339°K	150°F	339°K	151°F
5%		367	201	367	201
10		389	240	389	240
20		410	279	411	280
30		434	322	434	322
40		455	359	453	356
50		473	392	470	386
60		491	425	487	418
70		513	464	510	458
80		536	505	531	497
90		572	570	567	562
95		600	620	594	609
EP		670	747	662	733

FIGURE 17

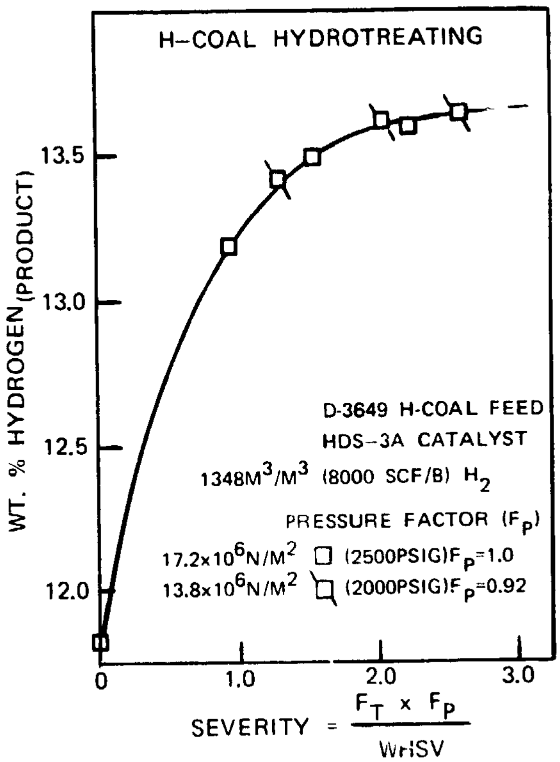
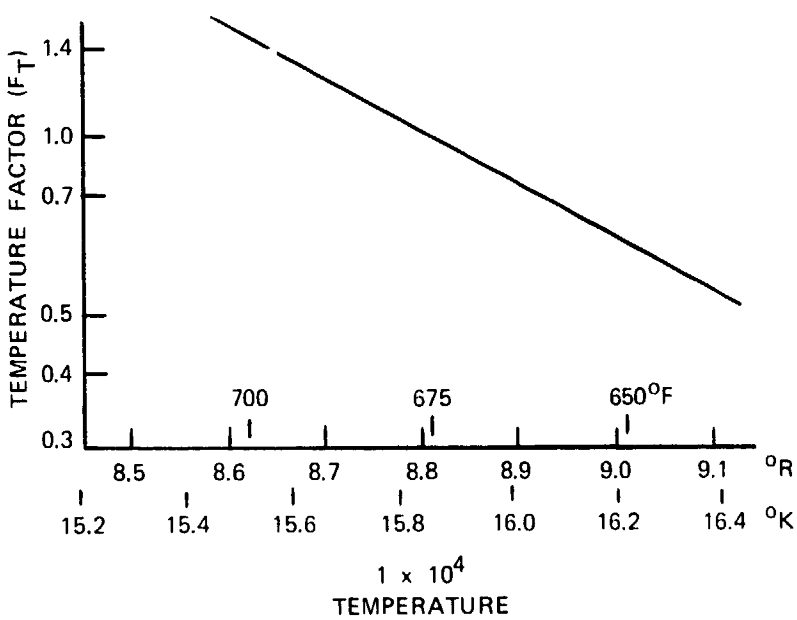


FIGURE 18

TEMPERATURE FACTOR FOR H–COAL HYDROGENATION



b. IBP-561^{o}K (550^{o}F) COED Syncrude Hydrotreating

The correlation between hydrogen content and operating severity shown in Figure 19 was developed from results obtained during the experimental run. This feed was a lower boiling fraction than the H-Coal sample correlated in Figure 17. Therefore, as a comparison of the two figures shows, the specified high hydrogen content of 13.5 percent was not as close to the saturation limit for the COED fraction as for the H-Coal fraction. However, despite the close approach to the saturation limit and a lower feed hydrogen content, less severe operating conditions were required to meet product specifications with the H-Coal feed than with this COED sample.

A curve depicting the effect of temperature on the hydrogenation of IBP-561^{o}K (550^{o}F) COED oil has been presented in Figure 20. This curve is not the straight line generally associated with Arrhenius plots. However, any effects of cracking at higher temperatures, which would increase product hydrogen content, have not been excluded from the relationship. Differences between the distillations of the products show a significant increase in cracking at the higher temperature. Cracking of C-C bonds results in products with a higher H/C ratio. If the activation energy of the hydrocracking reaction is greater than that of hydrogenation of aromatic compounds, a temperature coefficient curve for the overall reaction of the observed shape would result. This relationship of apparent hydrogenation rates at 616 (650) and 644^{o}K (700^{o}F) was later substantiated by results of the production run.

Figure 21 shows the relationship between hydrogen consumption and product hydrogen content.

Analyses of the high and low severity hydrotreated products and the feedstock are shown in Table X.

The rates of catalyst deactivation observed during the production runs are unusually high, for no immediately apparent reason. If they were to continue, operation would only be possible for a few weeks before the catalyst activity had declined to the point that regeneration or catalyst replacement would be required. It is possible, however, that activity might stabilize at some lower value and permit runs of practical duration. Longer term aging studies would be required to resolve these questions.

TABLE X

FEED AND PRODUCT INSPECTIONS

IBP–561°K (550°F) COED SYNCRUDE

	FEED	LOW SEVERITY PRODUCT	HIGH SEVERITY PRODUCT
SAMPLE NO.	33439	33487	33478
GRAVITY Kg/M^3	887.7	851.4	832.8
(°API)	(27.9)	(34.7)	(38.4)
HYDROGEN, %	12.32	12.77	13.47
SULFUR, ppm	240	2.2	3.4
NITROGEN, ppm	3338	5	4
R.I. @ 20°C	1.49165	–	–

FIGURE 19

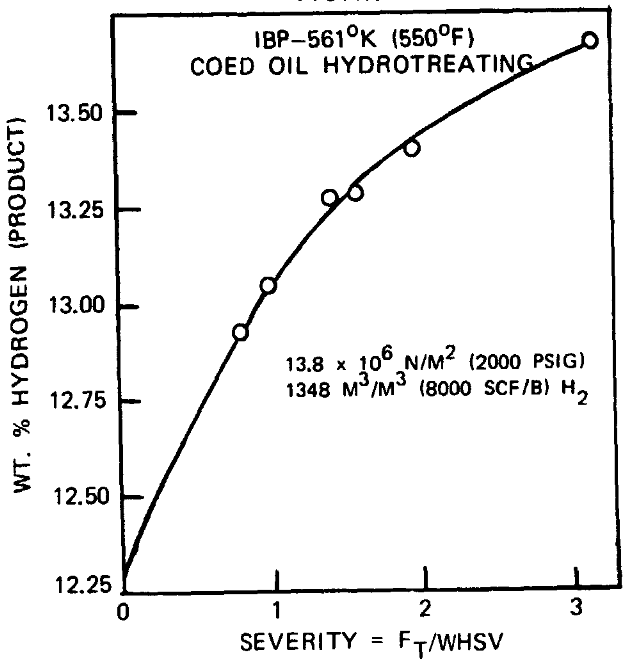


FIGURE 20
TEMPERATURE FACTOR FOR IBP-561°K (550°F)
COED OIL HYDROGENATION

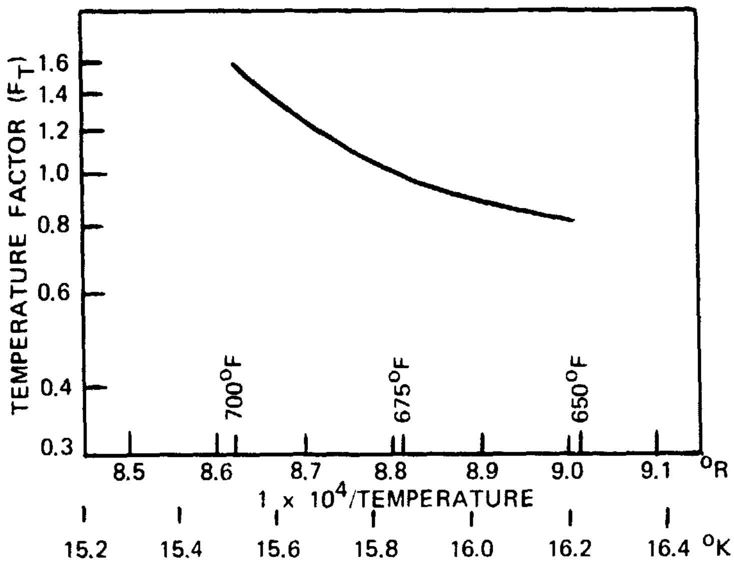
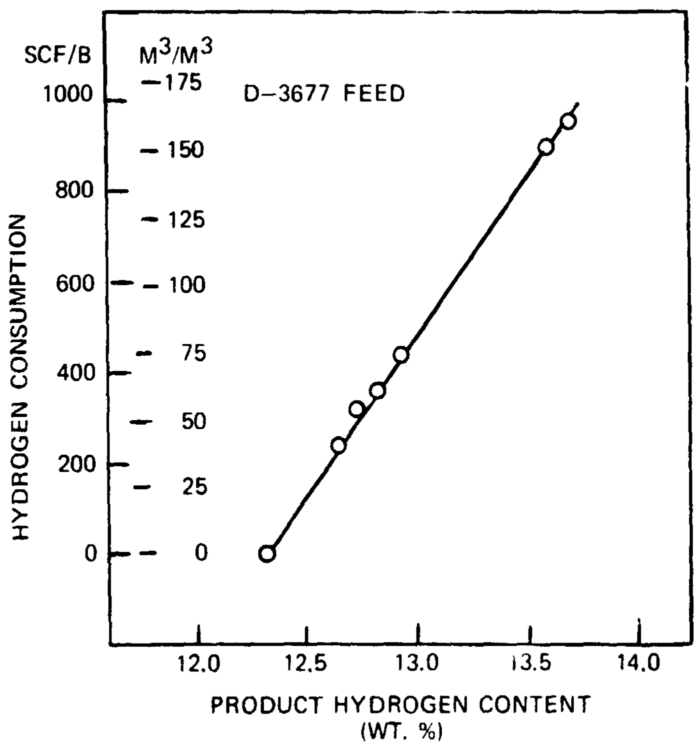


FIGURE 21
IBP-561°K(550°F) COED OIL HYDROTREATING
HYDROGEN CONSUMPTION RATE



c. Hydrotreating of 561-700^{o}K (550-800^{o}F) COED Syncrude

Because of the frequent reactor plugging and run restarts, adequate data to prepare a severity/conversion correlation was not obtained. It is possible, however to make a single point comparison between the severity required for the COED syncrude and the 616-783^{o}K (650-950^{o}F) shale fraction. At the conditions run (655^{o}K, 720^{o}F; 0.75 WHSV; 13.8 x 10^{6} N/m^{2}, 2000 PSIG; and 1348 m^{3}/m^{3}, 8000 SCF/B H_2) nitrogen removal from the COED syncrude was 95%, while shale oil denitrogenation would be 89% (Figure 4). However, if allowance is made for the almost tenfold higher feed nitrogen content and the 83^{o}K (150^{o}F) higher end point of the shale oil, we estimate that COED syncrude is in fact about 1.3 times more difficult to denitrogenate than shale oil.

The while solid material which was responsible for plugging the reactor was positively identified by x-ray diffraction as being predominantly ammonium chloride, with small quantities of iron salts and organic material also detected by microscopical examination. Analyses of the 561-700^{o}K (550-800^{o}F) COED oil feedstock and hydrotreated product for chlorine in Table XI show that chlorine was removed from the feedstock in the hydrotreating reactor, presumably as HCl, which reacted with ammonia to form a solid deposit of ammonium chloride in the cooler zone of the reactor exit. Filtration and molecular sieve drying treatments of the 561-700^{o}K (550-800^{o}F) hydrotreater feedstock were unsuccessful in preventing reactor plugging and, therefore, in removing chlorine. However, a water washing procedure utilizing equal volumes of water and 561-700^{o}K (550-800^{o}F) COED oil was found to reduce the chlorine content of the 561-700^{o}K (550-800^{o}F) fraction from 0.039 to 0.008 wt. %. This indicates that the chlorine was present as a water soluble compound which is reactive at the conditions of the hydrotreater. The origin of this material is unknown.

Feed and composite product analyses are shown in Table XI. Hydrogen consumption was approximately 320 m^{3}/m^{3} (1900 SCF/B). A catalyst deactivation rate was difficult to calculate as a result of the reactor plugging problems which were encountered. However, there was a noticeable loss in catalyst activity, as is apparent from the increase in product nitrogen values from $\sim$175 to $\sim$300 ppm, recorded during the run. The nitrogen content of the composited product was 237 ppm. In addition, the G.C. simulated distillations show that appreciable cracking occurred, resulting in approximately 20% conversion to 561^{o}K (550^{o}F) and lighter material. Total liquid product yield, however, was essentially 100 percent.

TABLE XI

COED 561-700°K (550-800°F) HYDROTREATING
PRODUCTION RUN

	FEEDSTOCK		COMPOSITE PRODUCT	
SAMPLE NO.	33358		33386	
GRAVITY Kg/M^3	951.6		916.4	
(°API)	(17.2)		(22.9)	
% SULFUR	0.025		0.002	
% HYDROGEN	10.63		11.91	
PPM NITROGEN	3578		237	
% CHLORINE	0.039		0.011	
DISTILLATION (G.C.)	°K	°F	°K	°F
IBP	560	548	379	222
5%	571	569	507	453
10	576	578	537	507
20	589	601	564	556
30	602	625	581	586
4C	616	650	597	616
50	630	675	615	647
60	644	699	632	678
70	658	725	650	710
80	673	752	669	744
90	694	789	691	785
95	708	815	705	809
EP	739	871	733	860

2. Hydrocracking of the 561-700^oK (550-800^oF) Fraction of COED Syncrude

Since the conversions to 616^oK (650^oF)- were too high in the experimental runs to be determined accurately (∿95%), and catalyst activity was constantly changing during the production run (Table XII), an indirect approach was necessary to derive the kinetics of the hydrocracking reaction. Using the experimental run data, a temperature coefficient of reaction was obtained for the first order rate constants of conversion to 472^oK (390^oF)-. Using this temperature coefficient, catalyst activity for conversion to 472^oK (390^oF)- as a function of time on stream during the production run was calculated. This activity correlation is shown in Figure 22. Assuming that activity for conversion to 616^oK (650^oF)- products was proportional, a temperature coefficient for conversion to 616^oK (650^oF)- products was calculated (Figure 23), and the first order correlation for conversion to 616^oK (650^oF)- incorporating these factors is shown in Figure 24.

The activity, α, is defined as the relative WHSV required to obtain constant conversion. At the end of the test, catalyst activity was down to 0.13 relative to the activity observed during the experimental test. This rate of catalyst deactivation would be a serious obstacle to any commercial application of this process. It is normal, with this catalyst system, to have a rate of activity decline at the beginning of a run period that is relatively greater than is observed later in the run. However, in this case we have an activity decline of 75% in 350 hours (neglecting the initial deactivation due to the HDN catalyst malfunction), which is excessive. Whether this activity decline would lessen and the catalyst stabilize if the run was continued beyond 350 hours cannot be predicted. A reduction in the feed endpoint to 644-672^oK (700-750^oF) may be one possible way to mitigate this problem.

The activity decline also affected product distribution. As temperature was increased to maintain conversion constant at ∿80 wt. % to 616^oK (650^oF), lighter products (422^oK(300^oF)) increased at the expense of the heavier, primarily 422-472^oK (300-390^oF). This effect is shown in Figure 25.

Because most of the production run was made at a constant conversion, 80%, the component yields and H_2 consumption relative to conversion cannot be defined. At 80% conversion to 616^oK-(650^oF), H_2 consumption was ∿227-236 m^3/m^3 (∿1350-1400 SCF/B).

Due to some confusion as to the exact weights of total feed and product, the overall yield on feed of the hydrocrackate was assumed to be 95%, which was the average yield of the weight balanced tests made during the production run.

The product from the production run was composited, and the boiling point distribution of the 311°K+ (100°F+) liquid product as a function of wt. % on hydrocracker feed is shown in Figure 26. The 311-616°K (100-650°F) product was produced in 70.2 wt. % yield on feed, 27.1% on COED syncrude; and the 422-561°K (300-550°F) in 26 wt. % yield on feed, 10.0% on syncrude.

3. Final Product Yields and Analyses

a. H-Coal Products

WT. % YIELD ON TOTAL H-COAL SYNCRUDE

(Low Yield Coal Syncrude Samples)

	LOW SEVERITY				HIGH SEVERITY			
Sample No.	33416	33417	33419	33418	33430	33431	33433	33432
Boiling Range, °K	311-616	394-616	311-561	394-561	311-616	394-616	311-561	394-561
, °F	100-650	250-650	100-550	250-550	100-650	250-650	100-550	250-550
310-422°K (100-300°F)	9.34	3.37	9.34	4.39	9.34	3.16	9.34	3.37
422-561°K (300-550°F)	24.71	24.71	24.71	24.71	25.10	25.10	25.10	25.10
561-616°K (550-650°F)	4.86	4.86	-	-	4.47	4.47	-	-
TOTAL	38.91	32.94	34.05	29.10	38.91	32.73	34.44	28.47

Analyses of all final product samples are given in Table XIII.

b. COED Products

WT. % YIELD ON TOTAL COED SYNCRUDE

(High Yield Coal Syncrude Samples)

	LOW SEVERITY				HIGH SEVERITY			
Sample No.	33516	33517	33519	33518	33502	33503	33505	33504
Boiling Range, °K	311-616	394-616	311-561	394-561	311-616	394-616	311-561	394-561
, °F	100-650	250-650	100-550	250-550	100-650	250-650	100-550	250-550
310-422°K (100-300°F)	16.31	5.78	16.31	5.92	16.31	5.18	16.31	5.28
422-561°K (300-550°F)	37.96	37.96	37.96	37.96	37.65	37.65	37.65	37.65
561-616°K (550-650°F)	8.47	8.47	-	-	8.78	8.78	-	-
TOTAL	62.74	52.21	54.27	43.88	62.74	51.61	53.96	42.93

TABLE XII

561-700°K (550-800°F) COED SYNCRUDE HYDROCRACKING

13.8×10^6 N/M^2 (2000 PSIG), 1685 M^3/M^3 (10,000 SCF/B) H_2

	EXPT'L RUN		PRODUCTION RUN			
TEST NO.	1	2	1	2	3	4
HOURS ON OIL	–	–	48	144	304	328
TEMP. HDN °K	644	644	644	644	655	655
HDN (°F)	(700)	(700)	(700)	(700)	(720)	(720)
HCK °K	619	607	608	613	633	626
HCK (°F)	(654)	(634)	(635)	(644)	(680)	(668)
WHSV						
HDN REACTOR	1.02	1.01	1.04	1.05	1.38	1.35
HCK REACTOR	.97	.96	.99	1.00	1.31	1.28
YIELDS, WT. % ON FEED						
C_3–	1.74	1.01	0.73	0.66	1.31	0.66
C_4	10.00	5.14	3.11	3.52	6.64	4.15
C_5	9.64	4.72	2.46	3.02	5.15	4.12
310-422°K (100-300°F)	48.80	40.85	22.76	27.58	27.41	25.27
422-561°K (300-550°F)	33.26	40.34	32.61	28.54	24.85	18.90
561-616°K (550-650°F)	0	7.64	19.93	18.79	17.02	22.32
616+°K (650+°F)	0	3.36	20.69	20.07	19.80	26.40
H_2 CONS., WT. %	3.44	3.07	2.33	2.22	2.22	1.85

FIGURE 22

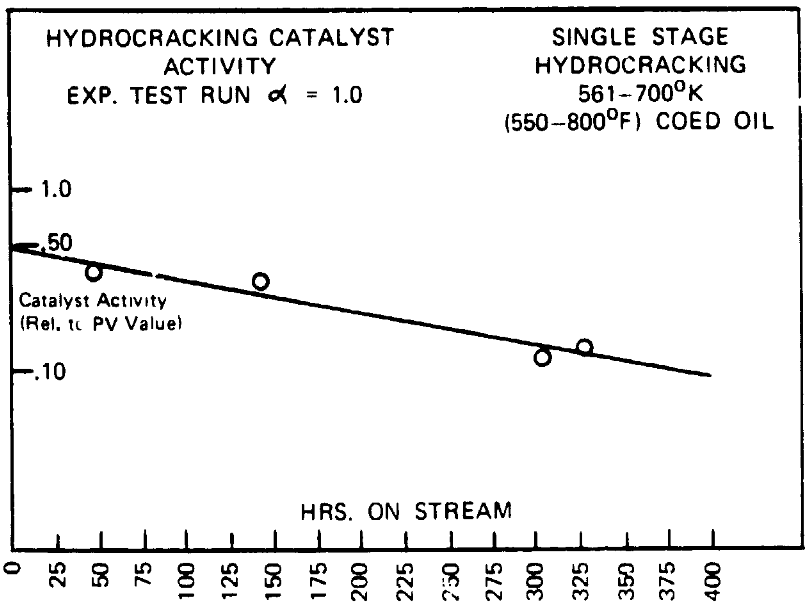


FIGURE 23

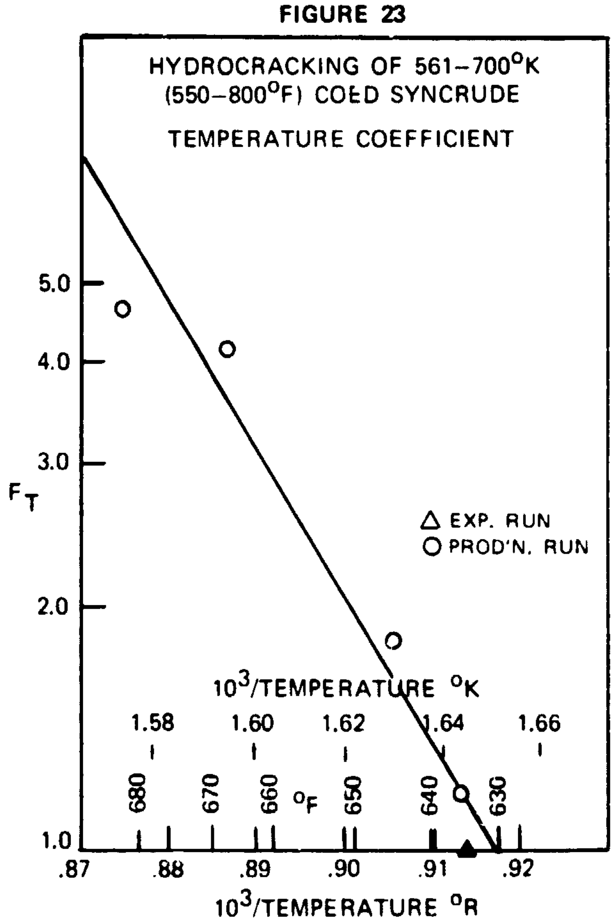


FIGURE 24

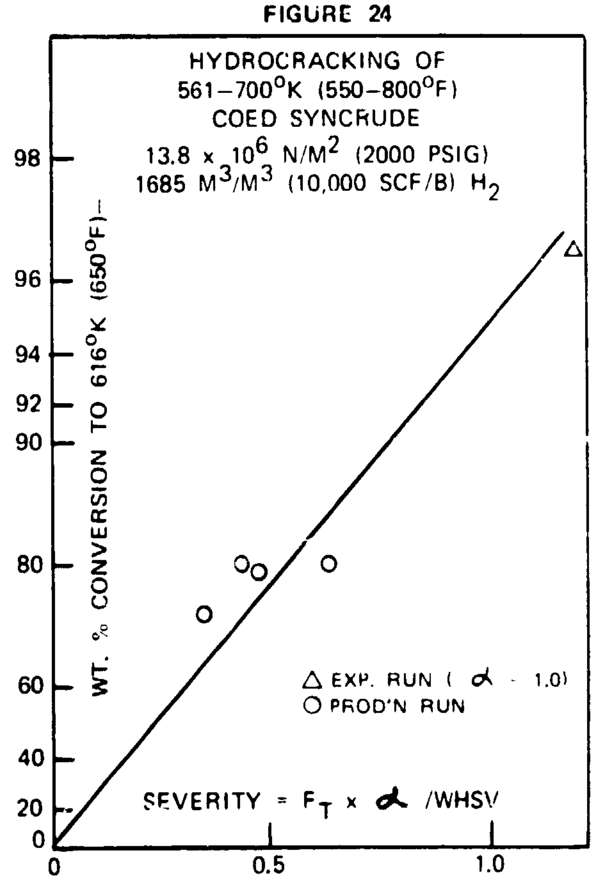


FIGURE 25

HYDROCRACKING OF 561–700°K (550–800°F)–
COED OIL YIELDS,
WT. % OF 616°K (650°F)–PRODUCT
~ 80 WT. % CONVERSION TO 616°K–

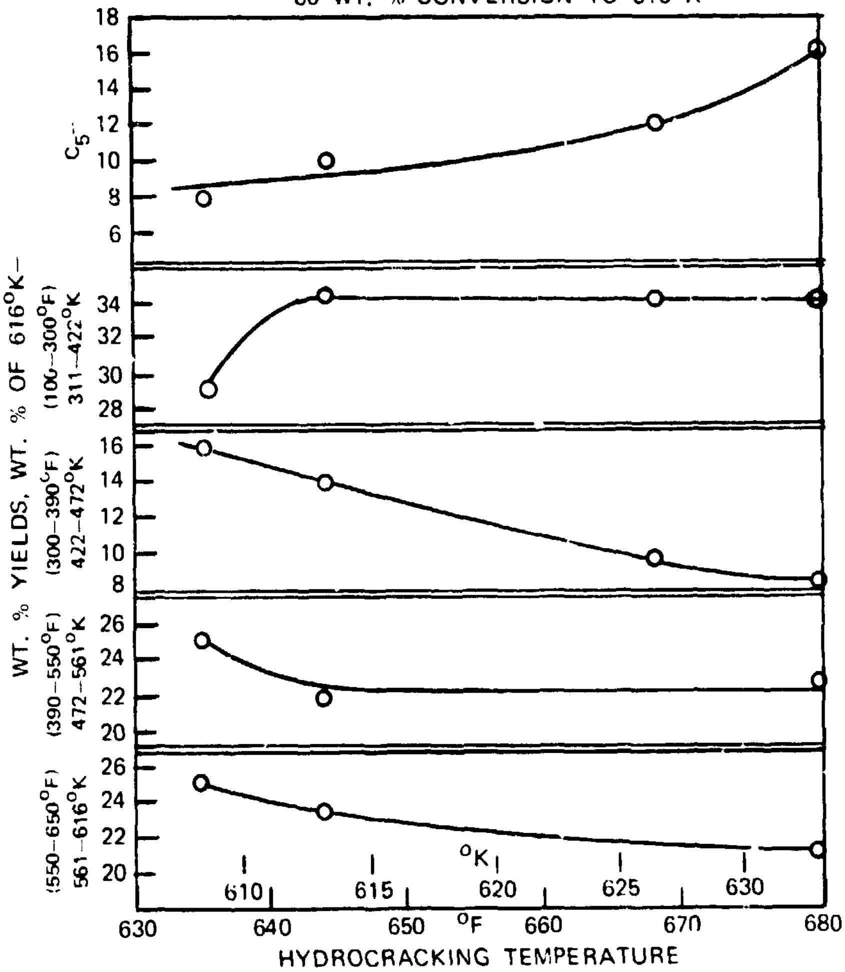
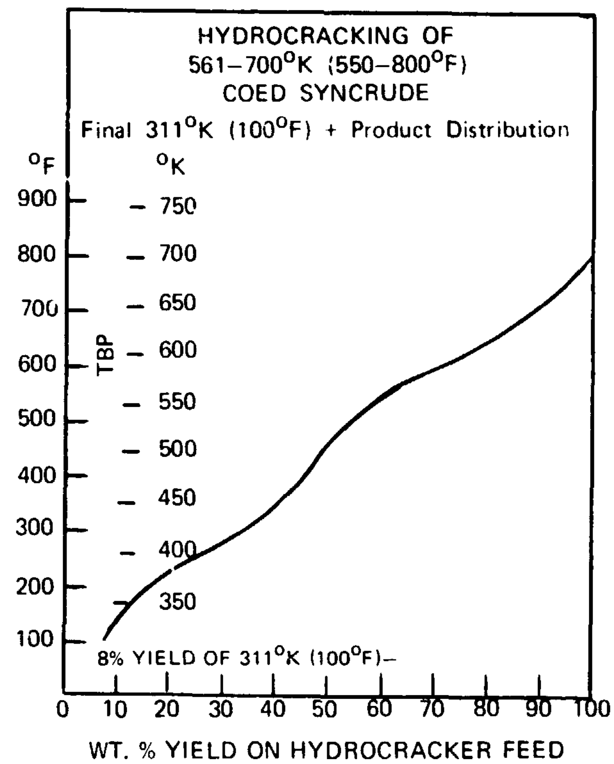


FIGURE 26



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The yield of 422-561°K (300-550°F) product falls slightly short of the 40 wt. % on syncrude as called for in the original plan. Once again, as described in Section III-B-4 on sources of additional yield from shale oil, hydrocracking of the 561-700°K (550-800°F) COED oil to 100% conversion to 616°K (650°F) by recycle to extinction of the 616°K+ (650°F+) portion would be possible, and would be probably practiced commercially. In that case, we would expect the following total yields on syncrude:

Fraction	Wt. % Yield
311-422°K (100-300°F)	17.95
422-561°K (300-550°F)	44.72
561-616°K (550-650°F)	9.04
TOTAL	71.71

Analyses of all final product samples are given in Table XIII.

TABLE XIII (p. 1)

COAL SYNCRUDE PRODUCT DISTILLATIONS (ASTM D-86)

LOW YIELD PRODUCTS

SAMPLE NO.	33416		33417	33418		33419		33430		33431		33432		33433	
	°K	°F		°K	°F	°K	°F	°K	°F	°K	°F	°K	°F	°K	°F
IBP	376	218	No	416	290	380	225	383	230	424	304	424	304	380	224
5%	399	258	Result	432	319	400	261	402	265	436	325	438	329	394	250
10	406	272		437	328	410	278	411	280	440	332	443	338	403	266
15	411	281	Too	441	334	417	292	416	290	444	340	447	346	411	280
20	422	301	Much	444	339	425	305	425	305	449	349	452	355	419	295
30	439	331	Foaming	453	356	439	331	439	330	457	363	461	371	437	327
40	455	360		462	372	452	355	454	357	466	379	470	387	457	364
50	469	384		470	387	464	375	468	383	475	395	479	402	470	386
60	483	410		481	406	475	395	482	409	489	420	487	418	480	404
70	499	438		496	434	486	416	497	436			499	438	491	425
80	521	479		500	440	502	444	521	478	Too		512	462	505	449
90	559	547		516	469	524	484	557	544	Much		532	499	530	495
95	604	628		535	504	547	526	599	619	Foaming		544	519	542	516
EP	624	663		550	531	557	543	615	648			545	522	558	545

HIGH YIELD PRODUCTS

SAMPLE NO.	33502		33503		33504		33505		33516		33517		33518		33519	
	°K	°F	°K	°F	°K	°F	°K	°F	°K	°F	°K	°F	°K	°F	°K	°F
IBP	360	188	425	305	427	309	360	189	362	192	425	305	424	304	360	189
5%	392	247	439	330	439	331	390	243	392	246	439	330	442	336	390	243
10	402	264	444	340	443	338	400	260	403	266	445	342	447	345	400	261
15	411	280	451	352	449	349	405	270	413	284	454	358	452	355	406	271
20	422	300	465	377	455	359	415	288	424	303	461	371	457	364	415	288
30	444	339	474	393	466	379	435	323	447	345	476	398	470	387	437	328
40	467	381	487	417	477	400	455	359	472	390	493	428	482	409	459	366
50	486	416	500	440	489	420	474	394	491	425	505	450	494	429	477	400
60	501	443	540	512	498	437	489	421	508	455			502	445	491	425
70	517	471	552	534	507	454	500	441	522	480	Too		511	461	505	449
80	535	503	570	567	517	471	511	461	539	510	Much		520	477	515	467
90	562	553	580	584	529	492	525	486	564	556	Foaming		529	493	526	487
95	582	589	589	601	539	510	536	505	584	591			537	507	535	503
EP	592	606	593	608	551	533	557	544	591	605			551	532	553	536

TABLE XIII (p. 2)

	H–COAL LOW YIELD PRODUCTS								COED HIGH YIELD PRODUCTS							
	LOW SEVERITY				HIGH SEVERITY				HIGH SEVERITY				LOW SEVERITY			
BOILING RANGE, °K	IBP-616	394-616	394-561	IBP-561	IBP-616	394-616	394-561	IBP-561	IBP-616	394-616	394-561	IBP-561	IBP-616	394-616	394-561	IBP-561
(°F)	(IBP-650)	(250-650)	(250-550)	(IBP-550)	(IBP-650)	(250-650)	(250-550)	(IBP-550)	(IBP-650)	(250-650)	(250-550)	(IBP-550)	(IBP-650)	(250-650)	(250-550)	(IBP-550)
SAMPLE NUMBER	33416	33417	33418	33419	33430	33431	33432	33433	33502	33503	33504	33505	33516	33517	33518	33519
SPECIFIC GRAVITY KG/M^3	849.3	865.4	856.5	841.3	833.8	848.8	846.8	831.4	825.5	845.8	836.8	816.5	835.8	858.6	849.3	827.0
REID VAPOR PRESSURE N/M^2	1380	–	–	1034	1724	–	–	3103	5861	–	–	5861	5861	–	–	7240
(PSI)	(0.20)	–	–	(0.15)	(0.25)	–	–	(0.45)	(0.85)	–	–	(0.85)	(0.85)	–	–	(1.05)
FLASH POINT, °K	–	312	309	–	–	312	314	–	–	313	314	–	–	319	313	–
(°F)	–	(102)	(96)	–	–	(102)	(106)	–	–	(104)	(106)	–	–	(114)	(104)	–
FREEZING POINT, °K	251	237	217	211	255	246	225	207	242	239	220	215	242	256	221	216
(°F)	(–8)	(–32)	(–68)	(–79)	(0)	(–17)	(–54)	(–86)	(–23)	(–30)	(–64)	(–72)	(–23)	(+2)	(–62)	(–70)
VISCOSITY @ 239°K(-30°F),CS	Solid	16.99	6.785	5.162	9.757	15.91	9.102	6.264	Solid	19.25	9.676	5.565	Solid	Solid	9.851	5.586
NET HEAT OF COMBUSTION (cal/g)	10,363	10,248	10,303	10,340	10,450	10,462	10,462	10,421	10,488	10,534	10,484	10,547	10,328	10,427	10,401	10,486
EXISTING GUM, mg	6.0(1)	74.0(1)	92.0(2)	10.2(2)	4.8(1)(3)	110.8(1)	11.2(2)	9.8(2)	0.8(1)	23.0(1)	6.6(2)	7.6(2)	1.6(1)	21.2(1)	2.4(2)	3.2(2)
SMOKE POINT	14	15	15	16	24	21	24	25	20	20	24	27	16	14	16	19
AROMATICS, %	29.7	33.8	30.9	26.3	5.9	6.7	5.8	5.5	9.3	11.6	7.2	5.4	22.4	28.5	25.2	20.1
OLEFINS, %	1.2	1.8	1.4	1.2	1.3	1.4	1.0	0.9	0.7	1.1	0.9	0.5	0.6	1.2	0.8	0.5
NAPHTHALENES, %	0.54	0.66	0.31	0.27	0.064	0.077	0.065	0.055	0.49	0.62	0.13	0.11	0.68	0.86	0.38	0.31
HYDROGEN, %	12.73	12.47	12.64	12.79	13.56	13.26	13.31	13.73	13.53	13.44	13.63	13.69	13.07	12.88	12.96	13.24
NITROGEN, ppm	5	6	6	1	1	1	1	1	2	2	2	2	3	2	2	2
TOTAL SULFUR, ppm	3.7	3.7	1.0	0.9	5.4	4.7	0.8	1.0	3.1	3.3	1.0	1.3	2.9	1.0	0.7	1.1
MERCAPTANS, ppm	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
OXYGEN, %	0.11	0.09	0.06	0.10	0.04	0.06	0.03	0.04	0.05	0.05	0.05	0.03	0.03	0.03	0.03	0.03
THERMAL STABILITY	4+	4+	4+	3	0	1	0	1	0	3	2	1	0	3	4	0

(1) D-381 STEAM JET METHOD @ 506°K (450°F)
(2) D-381 AIR JET METHOD @ 428°K (311°F)
(3) THIS SAMPLE TOO VOLATILE FOR 506°K BATH AND BOILED OVER. 2377.6 mg. WAS RESULT WITH AIR JET @ 428°K.

V. DISCUSSION OF RESULTS

The objective of this project was the production of samples of jet fuel of various properties from shale oil and coal syncrudes, using conventional petroleum processing technology. These samples were analyzed to assess their potential for use as jet fuel. No attempt was made to optimize the processing systems, either technically or economically.

The program has demonstrated that products which may be useful as jet fuels can be produced from these petroleum substitutes by hydrotreating and hydrocracking at suitably severe conditions. The products from high severity hydrotreating of shale oil appear to be more suitable than those from low severity processing. Besides the high nitrogen content of the latter, which could result in undesirably high NO_x emissions, existing gum and smoke point are also poor. Long term storage stability may also be a problem. The hydroprocessing technology for the production of these materials is largely developed and does not appear to present any severe technical problems.

The samples produced from the coal syncrudes at high hydrogenation severity would appear to be less desirable as jet fuels, primarily with respect to smoke point. The low severity products are somewhat poorer in all respects. The technology for processing of coal syncrudes is not as completely developed as that for shale oil, and some additional process research and development would be required, particularly in the area of catalyst activity and stability.

These processes, however, are subject to severe economic problems. High capital and processing costs are associated with the high pressures and low space velocities required. In addition, large quantities of hydrogen are consumed in order to yield reasonable quality products. Current costs for manufactured hydrogen by steam reforming of fuel gas or naphtha are ∿\$2-\$2.50 per 168.5 cubic meters (thousand cubic feet). Based on this value, the hydrogen cost for hydrotreating the existing 311-616^{o}K (100-650^{o}F) fraction of shale or coal syncrude is ∿\$2.50/.16 m^3 (Bbl), (185 m^3/m^3, 1100 SCF/B). In the case of coal syncrude, this is in addition to the substantial hydrogen consumption of the liquefaction process itself.

If heavier fractions are hydrocracked, hydrogen costs increase rapidly. In the shale oil case, it increases to ∿\$4 per .16 m^3 (barrel) of product (292 m^3, 1735 SCF), or \$6.50 per incremental .16 m^3 (barrel) of product. For coal syncrude, overall hydrogen cost becomes ∿\$5 per .16 m^3 (barrel) of product (393 m^3, 2330 SCF), or ∿\$8 per incremental .16 m^3 (barrel) of product—again in addition to the hydrogen consumed in the liquefaction process.

The above considerations emphasize the importance of optimization of these processes. Both the hydrotreating-hydrocracking system and alternative process schemes require additional data and evaluation. Options which have potential to significantly reduce hydrogen costs would be of particular interest, such as improved processes for the production of hydrogen from residual fractions or coke. Mild hydrotreating followed by fluid catalytic cracking may be an attractive alternative to hydrocracking, reducing both hydrogen consumption and capital requirement, albeit at some reduction in yield.

Based upon hydrogen consumption and product quality, it appears that jet fuel production from shale oil would be preferred to using coal as the original hydrocarbon source. A complete evaluation of the relative costs of these alternatives should be made, and future work concentrated upon the more efficient of the two.

VI. SUMMARY OF RESULTS

The objective of this project was the production of samples of jet fuel of various properties from shale oil and coal syncrudes, using conventional petroleum processing technology. These samples were analyzed to assess their potential for use as jet fuel. The program has demonstrated that products which may be useful as jet fuels can be produced from these petroleum substitutes by hydrotreating and hydrocracking at suitably severe conditions.

Some promising products were produced from TOSCO II shale oil by hydrotreating a 311-616°K (100-650°F) boiling fraction over $NiMo/Al_2O_3$ catalyst at 652°K (715°F), 1.5 WHSV, 13.8×10^6 N/m^2 (2000 PSIG) and 1348 m^3/m^3 (8000 SCF/B) H_2. Processing at less severe conditions (i.e., lower temperature and/or higher WHSV) yielded a marginal product with a high nitrogen content, high existing gum and high smoke point.

An additional quantity of jet fuel was produced by hydrocracking the 616-783°K (650-950°F) fraction of the shale oil. This involved two successive hydrodenitrogenation steps at the following conditions:

	1	2
Temperature, °K (°F)	675 (755)	639 (690)
WHSV	0.36	1.0
N/m^2 (PSIG)	13.8×10^6 (2000)	13.8×10^6 (2000)
m^3/m^3 (SCF/B) H_2	1348 (8000)	1685 (10,000)

These were followed by the hydrocracking step proper at 622°K (660°F), 0.75 WHSV, 13.8×10^6 N/m^2 (2000 PSIG), and 1685 m^3/m^3 (10,000 SCF/B) H_2. The 311-616°K (100-650°F) product from this processing sequence was combined with the hydrotreated 311-616°K (100-650°F) cut described in the preceding paragraph to produce another set of samples.

Data were also obtained that indicated another source of increased yield would be delayed coking of the 783°K (950°F)+ shale oil bottoms, followed by hydrotreating and hydrocracking of the coker liquid product. No samples were actually produced by this means, however.

A sample of H-Coal process syncrude was obtained which consisted of a 311-616°K (100-650°F) boiling range liquid, and a solid 700°K (800°F)+ bottoms product which was deemed impractical to process. The liquid was hydrotreated at initial conditions of 630°K (675°F), 0.5 WHSV, 17.2×10^6 N/m^2 (2500 PSIG) and 1348 m^3/m^3 (8000 SCF/B) H_2, but substantial catalyst deactivation was observed during the process period. The product was of reasonably good quality although smoke point was low. Lower severities produced correspondingly poorer product.

A syncrude made from Utah coal by the COED process was also obtained and processed. The 311-561^{o}K (100-550^{o}F) fraction was hydrotreated at 641^{o}K (695^{o}F), 0.5 WHSV, 13.8 x 10^6 N/m^2 (2000 PSIG) and 1348 m^3/m^3 (8000 SCF/B). The 561-700^{o}K (550-800^{o}F) fraction was hydrocracked in three steps as follows:

	HDN-1	HDN-2	HCK
Temperature, ^{o}K (^{o}F)	658 (725)	644 (700)	608 (635)
WHSV	0.75	1.05	1.0
N/m^2 (PSIG)	13.8 x 10^6 (2000)------------	------------	------------
H_2, m^3/m^3 (SCF/B)	1348 (8000)	1685 (10,000)------	------

Again, these were initial conditions and severe catalyst deactivation was observed during all processing of the COED syncrude.

The hydrotreated 311-561^{o}K (100-550^{o}F) fraction was combined with the 311-616^{o}K (100-650^{o}F) product from hydrocracking and a potential jet fuel product was obtained, although smoke point was somewhat low.

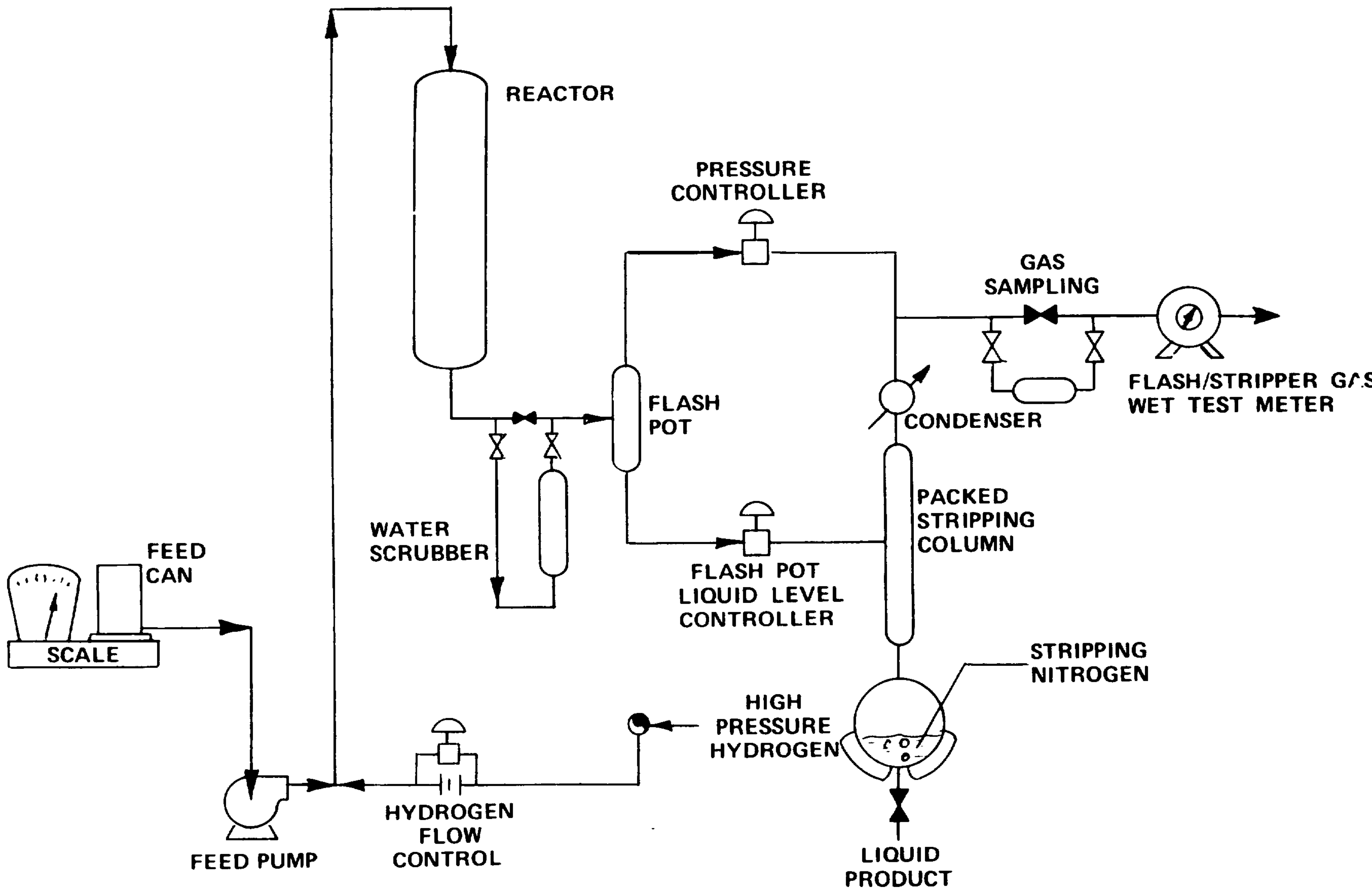
Concluding Remarks

The hydroprocessing technology required to produce potential jet fuels from shale oil is largely developed, and does not appear to present any severe technical problems. The products from coal syncrude processing are of somewhat poorer quality, and the technology is not as completely developed. Some additional process research and development would be required, particularly in the area of catalyst activity and stability.

These processes are, however, subject to severe economic problems. High capital and operating costs are associated with the high pressures and low space velocities required. In addition, large quantities of hydrogen are consumed in order to yield reasonable quality products. Based on a cost of manufactured hydrogen of $2 per 168.5 cubic meters (thousand cubic feet), the cost of hydrogen for shale oil processing would be $2.50-$4 per .16 m^3 (barrel) of product, depending on yield obtained. For coal syncrude processing, the costs are $2.50-$5 per .16 m^3 (barrel) of product, in addition to the substantial hydrogen consumption of the liquefaction process itself.

The above considerations emphasize the importance of technical and economic optimization of these processes, a task which was not a part of this program. Based upon hydrogen consumption and product quality, however, it appears that shale oil would be preferred to coal as the original hydrocarbon source for jet fuel production.

Figure 27
Hydrotreating Unit Flow Diagram



VII. REFERENCES

(1) Shaw, H., et. al., "Evaluation of Methods to Produce Aviation Turbine Fuels from Synthetic Crude Oils - Phase I", Report to U.S. Air Force under Contract F33615-74-C-2036, March, 1975.

(2) Eisen, F. S., "Preparation of Gas Turbine Engine Fuel from Synthetic Crude Oil Derived from Coal - Phase I", Report to U.S. Navy under Contract N00140-74-C-0568, Oct. 15, 1974.

(3) Greene, M. F., et. al., "Low Sulfur Synthetic Crude Oil from Coal", Presented at ACS National Meeting, Div. of Fuel Chemistry, Los Angeles, California, April 1974.

(4) Wachtel, S. J., et. al., "Evaluation of Hydrotreated COED Syncrude". Report to FMC Corp., Subcontract 1212-2, Prime Contract 14-32-0001-1212, Dept. of Interior, Office of Coal Research, Jan., 1973.